Chemical analysis of the interface between hybrid organic−inorganic perovskite and atomic layer deposited Al2O3

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Chemical Analysis of the Interface between Hybrid Organic–Inorganic Perovskite and Atomic Layer Deposited Al₂O₃

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ABSTRACT: Ultrathin metal oxides prepared by atomic layer deposition (ALD) have gained utmost attention as moisture and thermal stress barrier layers in perovskite solar cells (PSCs). We have recently shown that 10 cycles of ALD Al₂O₃ deposited directly on top of the CH₃NH₃PbI₃₋ₓClₓ perovskite material, are effective in delivering a superior PSC performance with 18% efficiency (compared to 15% of the Al₂O₃-free cell) with a long-term humidity-stability of more than 60 days. Motivated by these results, the present contribution focuses on the chemical modification which the CH₃NH₃PbI₃₋ₓClₓ perovskite undergoes upon growth of ALD Al₂O₃. Specifically, we combine in situ infrared (IR) spectroscopy studies during film growth, together with X-ray photoelectron spectroscopy (XPS) analysis of the ALD Al₂O₃/perovskite interface. The IR-active signature of the NH₃⁺ stretching mode of the perovskite undergoes minimal changes upon exposure to ALD cycles, suggesting no diffusion of ALD precursor and co-reactant (Al(CH₃)₃ and H₂O) into the bulk of the perovskite. However, by analyzing the difference between the IR spectra associated with the Al₂O₃ coated perovskite and the pristine perovskite, respectively, changes occurring at the surface of perovskite are monitored. The abstraction of either NH₃ or CH₃NH₂ from the perovskite surface is observed as deduced by the development of negative N = H bands associated with its stretching and bending modes. The IR investigations are corroborated by XPS study, confirming the abstraction of CH₃NH₂ from the perovskite surface, whereas no oxidation of its inorganic framework is observed within the ALD window process investigated in this work. In parallel, the growth of ALD Al₂O₃ on perovskite is witnessed by the appearance of characteristic IR-active Al–O–Al phonon and (OH)−–Al=O stretching modes. Based on the IR and XPS investigations, a plausible growth mechanism of ALD Al₂O₃ on top of perovskite is presented.

KEYWORDS: perovskite, atomic layer deposition, Al₂O₃, infrared spectroscopy, X-ray photoelectron spectroscopy

INTRODUCTION

Three dimensional hybrid organic–inorganic perovskites with the general chemical formula ABX₃ (A = CH₃NH₃⁺, HC–(NH₂)₂⁺, B = Pb, Sn, and X = I, Cl, Br) are characterized by extremely appealing electronic and morphological characteristics which are dominated by the complex interactions interplaying between the organic moiety and the inorganic framework of the lattice. The most conventional perovskite, methylammonium lead iodide (CH₃NH₃PbI₃) has gained utmost attention in the photovoltaic (PV) community owing to the unprecedented device efficiencies demonstrated in the last eight years. However, the presence of the volatile CH₃NH₃⁺ component in its lattice structure makes this perovskite highly unstable against environmental exposure. Massive efforts have been made to enhance the environmental stability of the perovskite solar cells (PSCs) by focusing on more stable perovskite compositions and/or adopting the approach of interface engineering. In the latter case, the application of atomic layer deposited (ALD) metal oxides in perovskite solar cells (PSCs) has led to significant advancement in enhancing the environmental stability of the fabricated devices. The work reported from our group showed that the implementation of ultrathin thermal ALD Al₂O₃ (<1 nm) directly on top of CH₃NH₃PbI₃₋ₓClₓ perovskite leads to an enhancement in both initial efficiency and humidity-stability of the PSC in comparison to the Al₂O₃-free reference device (humidity conditions ranging from 40 to 70% at room temperature).

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Kot et al. demonstrated the incorporation of room-temperature ALD Al₂O₃ on top of both fresh²³ and 50 days aged²⁴ CH₃NH₃PbI₃ perovskite to improve the power conversion efficiency (PCE) of the PSC and its ambient air stability. The applicability of ALD Al₂O₃ was extended also toward other perovskite chemistries in the work of Louidou et al., where an ALD Al₂O₃ layer was adopted to stabilize CsPbBr₃Iₓ₋ₓ and CsPbI₃ quantum dots.²⁵ In contrast to the above ALD Al₂O₃ processes which used trimethylaluminum (TMA) and H₂O vapor as the precursor and co-reactant respectively, Kim et al. utilized aluminum triisopropoxide and acetic acid in view of a water-free ALD Al₂O₃ process to passivate CH₃NH₃PbI₃ perovskite against a relative humidity of 85%, and also to improve the thermal stability of the films up to 250 °C.²⁶ Inspired by these seminal studies demonstrating Al₂O₃ effects directly on top of perovskites, the application of ALD has expanded further toward other metal oxides, among which directly on top of perovskites, the application of ALD has been studied with XRD and XPS to demonstrate the role of bulk and surface stability of the perovskite during ALD.¹⁷,³³,³⁷

Aforementioned intriguing results manifest that the growth of ALD metal oxides directly on top of the hybrid perovskites is challenging, and hence, motivate a detailed investigation of the interaction of perovskite with ALD precursors and co-reactants during the deposition of metal oxides on top. Understanding the factors governing perovskite chemical modifications and ALD growth behavior would enable the accomplishment of efficient and stable PSCs. In this regard, Choudhury et al. performed in situ Quartz Crystal Microbalance (QCM) and Fourier transform Infrared (IR) spectroscopy measurements on CH₃NH₃PbI₃Clₓ perovskite during its individual interactions with TMA and H₂O vapor at 75 °C. The results showed that TMA could continuouslyetch the perovskite at 75 °C, and at the same time could be more detrimental toward perovskite degradation than H₂O vapor exposure.³⁴ Work of Yu et al. focused on the nucleation of ALD metal oxides on top of the PCBM/perovskite layer.³⁵ Kot et al. implemented synchrotron X-ray photoelectron spectroscopy (XPS) to study the room-temperature ALD Al₂O₃/CH₃NH₃PbI₃Clₓ perovskite and showed the interaction of ALD precursors to occur only at the surface of the perovskite.³⁶ It was demonstrated that chemical changes at the CH₃NH₃PbI₃/Al₂O₃ interface could also alter the electronic properties of the perovskite. In situ valence-band XPS results showed changes in the position of the valence-band maximum (VBM) of CH₃NH₃PbI₃ with increase in the number of Al₂O₃ cycles.²³,²⁴ An additional, X-ray diffraction (XRD) and XPS were utilized to demonstrate the role of metal–organic precursor chemistry toward maintaining both bulk and surface stability of the perovskite during ALD.³⁷,³⁵,³⁷

In this work, we perform in situ IR spectroscopy on CH₃NH₃PbI₃Clₓ perovskite to study its structural and chemical modifications during the growth of ALD Al₂O₃ on top, employing TMA as the precursor and H₂O vapor as the co-reactant at 80 °C. We choose ALD Al₂O₃ for the present study as it is one of the well-established ALD metal oxides, and has already been demonstrated to work successfully in enhancing the stability of PSCs. The in situ IR results are complemented by XPS analysis carried out on the perovskite/ALD Al₂O₃ interface. Based on the XPS results, we discuss how the growth of ALD Al₂O₃ can initiate and then further develop on top of CH₃NH₃PbI₃Clₓ perovskite.

### EXPERIMENTAL SECTION

#### CH₃NH₃PbI₃Clₓ Perovskite Film Preparation.

The perovskite precursor solution is made by mixing lead acetate (Pb(CH₃COO)₂) lead chloride (PbCl₂) and methylammonium iodide (MAI) in dimethylformamide (DMF) as previously reported.³⁸ A ∼ 500 μm thick double-side polished Si (100) wafer (n-type doping, 30–50 Ω·cm) with native oxide is used as the substrate. The precursor solution is spin-coated inside a N₂ filled glovebox on one side of the double polished Si wafer at 3000 rpm for 60 s. The substrate is subsequently annealed at 130 °C for 10 min to form the perovskite layer.

#### ALD Process of Al₂O₃.

Al₂O₃ is deposited on top of the perovskite/Si substrate at 80 °C in a home-built ALD reactor, which is a high-vacuum system that is evacuated by a combination of a rotary and a turbomolecular pump to a base pressure of 10⁻⁶ mbar. The system has been extensively described in our previous work.³⁹ Each ALD cycle consists of a TMA dose of 0.08 s, followed by a purge of 4.0 s, then a H₂O vapor dose of 0.1 s, followed by a purge of 4.0 s. The thickness of the ALD Al₂O₃ layers on the c-Si substrate is characterized by spectroscopic ellipsometry (SE) using J.A. Woollam, Inc. M2000 UV ellipsometer and the growth per cycle (GPC) is determined to be 0.06 nm.

#### IR Spectroscopy.

The IR setup consists of a Bruker Vector 22 Fourier transform IR spectrometer with a mid-infrared light source (Globar ∼10 000–50 cm⁻¹). The substrate is mounted onto a sample manipulator (PREVAC, four axes manipulator), which enables for a controlled movement of the sample in all the X, Y, and Z directions. The perovskite/Si substrate is placed vertically with the IR beam, that is, at normal angle of incidence. KBr windows are used as entry and exit windows for the IR light. In order to prevent deposition on these windows, shutters are installed, and are opened only during the IR measurements. The intensity of the transmitted IR light is measured using a liquid N₂ cooled mercury cadmium tellurium (MCT) detector (Bruker D316) in a spectral range of 4000–700 cm⁻¹. The Vector 22 as well as the environment of the MCT detector is continuously purged with dry N₂ gas. In addition, before each measurement the reactor is pumped down to a base pressure of <5 × 10⁻⁶ mbar in order to minimize contributions from the gas phase species present inside the reactor to the measured transmittance spectra. The perovskite samples are exposed to vacuum conditions of 10⁻⁶ mbar for a maximum of 5 h during the experiments. All IR measurements performed in this work have been acquired with an average of 1024 scans, and with a resolution of 4 cm⁻¹. The infrared absorbance (A) has been calculated by A = log(I₁/I₀), where I₀ and I₁ are the measured transmittance of the sample after and before Al₂O₃ deposition, respectively. The approach adopted for calculating the absorbance on perovskite which is deposited on one side of the double polished Si wafer is schematically presented in Supporting Information (SI) Figure S1 (the absorbance difference between a perovskite/Si substrate and a Si substrate). It is to be noted that IR spectra measured on pressed pellets are known to sometimes suffer from artifacts, especially when the samples of interest are halide based, due to the possible hydrogen-bond interactions with the pellet materials like KBr and KCl.⁴⁰,⁴¹ Hence, in the present study, we have opted for double-side polished Si as the substrate.

#### XRD.

XRD analysis is carried out on the perovskite/Si and ALD Al₂O₃/perovskite/Si samples using a PANalytical X’Pert Pro MRD X-ray diffractometer using Cu Kα radiation (λ = 1.540598 Å) in the 2θ range 10–60° at a scanning rate of 1.5° min⁻¹. XPS. Ex situ XPS measurements are carried out right after the ALD Al₂O₃ deposition on perovskite. The perovskite/ALD Al₂O₃ samples are transferred to the XPS setup in N₂ filled containers (under dark conditions) and the time of exposure of the samples to ambient air is <5 min. The measurements are carried out in a Thermo Scientific K-
Alpha system, equipped with an Al X-ray source (Kα, 1486.6 eV) without any presputtering. Binding energy is corrected with respect to adventitious carbon (C 1s) at 284.8 eV. The peak fit results are obtained using Thermo Avantage software applying Powell fitting algorithm and Gauss-Lorentz Mix. The Al2O3 film thickness on top of the Si substrate (d_{Al2O3}) is calculated by measuring the attenuation of the silicon core level using eq 1, which is given as,

\[ I_s = I_o \exp\left(-\frac{d_{Al2O3}}{\lambda}\sin \theta \right) \]  

where, \( I_o \) is the photoelectron yield with Al2O3 on Si, \( I_s \) is the photoelectron yield without Al2O3 on Si, \( d \) is the Al2O3 thickness (nm), \( \lambda \) is the inelastic mean free path of the electron (nm), and \( \theta \) is the XPS takeoff angle (degree). \( I_s \) and \( I_o \) are obtained by integrating the area under the Si 2p peak (Si 0), avoiding the SiO 2 (Si^{4+}) contribution. The inelastic mean free path (IMFP) of electron is obtained from the NIST IMFP database using the TPP-2M formula.42 Similar procedure is utilized to calculate the thickness of ALD Al2O3. The XPS takeoff angle is 90°. It should be noted that the value of \( \lambda_{Al2O3} \) is dependent on the energy of the employed X-ray photons, binding energy of the element whose attenuation is monitored and also on the density of the overlayer. So, it is recommended to verify the thickness values obtained from XPS by additional characterization techniques such as, SE and transmission electron microscopy (TEM).

Transmission Electron Microscopy (TEM) and Elemental Mapping. Cross-sectional TEM samples of the stack comprising of perovskite/ALD Al2O3/Spiro-OMeTAD are prepared using a standard Focused Ion Beam liftout procedure. In the transfer step, the samples are mounted on molybdenum support grids upon which the final thinning is performed. The TEM studies are performed using a JEOL ARM 200 probe corrected TEM, operated at 200 kV, and equipped with a 100 mm² Centurio SDD energy dispersive X-ray spectroscopy (EDX) detector. EDX mappings of 256×256 full spectra are acquired using a 0.1 ms dwell time, summing up over 37, 128, and 105 full frame acquisitions. Quantification of the EDX maps is performed using standard k-factors.

## RESULTS AND DISCUSSION

Figure 1 shows the IR spectrum of a ~300 nm thick pristine CH3NH3PbI3-Clx perovskite film. The observed vibrational modes (summarized in Table 1) are in good agreement with those reported in literature.34,43-45 The most intense vibrational mode is marked by the symmetric and asymmetric N−H stretching modes (associated with NH3+) at 3132 and 3179 cm⁻¹, respectively. The absence of O−H stretching vibrations in the region of 3400−3700 cm⁻¹ indicates the absence of hydroxyl species (water, hydrates and hydroxide) in our pristine perovskite films.

Figure 2 shows the changes which the characteristic IR-active NH3+ stretching modes of the perovskite undergoes during consecutive cycles of ALD Al2O3. A decrease in both symmetric (3132 cm⁻¹) and asymmetric (3179 cm⁻¹) N−H stretching modes is evident upon increasing the number of Al2O3 cycles. At the same time, narrowing of the NH3+ stretch band is witnessed, which is accompanied by a minor shift of the symmetric N−H stretching mode toward higher frequencies. The observed simultaneous decrease and shift in the symmetric N−H stretching vibration can be explained by the interaction of water with the CH3NH3+ group of the perovskite. A similar behavior was observed by Müller et al. when the perovskite was exposed to a relative humidity (R.H.) of 13%.46 However, in contrast to the work of Müller et al., we do not observe the two well-defined peaks at around 3500 and 3450 cm⁻¹ (belonging to asymmetric and symmetric O−H stretching modes of H2O),47 indicating that diffusion of water molecules does not occur into the bulk of the perovskite. In the employed ALD Al2O3 recipe, the perovskite is exposed to consecutive H2O pulses of 1×10⁵ L which results in a significantly lower R.H. environment (maximum of 0.1%) in the ALD chamber.17 Hence, the interaction between H2O molecule and CH3NH3+ is rather weak during our H2O dosage step. This is in agreement with work of Li et al., where it was shown that H2O exposure of below 2×10⁵ L does cause degradation of CH3NH3PbI3.48 The IR results indicating negligible bulk decomposition of the perovskite are also shown that H2O exposure of below 2×10⁵ L does cause degradation of CH3NH3PbI3.48 The IR results indicating negligible bulk decomposition of the perovskite are also

Table 1. Characteristic IR-Active Vibrational Modes of the Pristine CH3NH3PbI3-Clx Perovskite

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Vibrational Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>3179</td>
<td>N−H stretch (asymmetric)</td>
</tr>
<tr>
<td>3132</td>
<td>N−H stretch (symmetric)</td>
</tr>
<tr>
<td>2958</td>
<td>C−H stretch (asymmetric)</td>
</tr>
<tr>
<td>2921</td>
<td>C−H stretch (symmetric)</td>
</tr>
<tr>
<td>1577</td>
<td>N−H bend (asymmetric)</td>
</tr>
<tr>
<td>1469</td>
<td>N−H bend (symmetric)</td>
</tr>
<tr>
<td>1249, 910</td>
<td>CH3NH3+ rock</td>
</tr>
<tr>
<td>962</td>
<td>C−N stretch</td>
</tr>
<tr>
<td>2817, 2711, 2488, 2375, 1840</td>
<td>CH3NH3+ resonant</td>
</tr>
</tbody>
</table>

Figure 1. IR spectrum of the pristine ~300 nm CH3NH3PbI3-Clx perovskite.

Figure 2. Change in the N−H stretching mode of the ~300 nm thick perovskite upon continuous exposure to cycles of ALD Al2O3.
corroborated by XRD. In Figure 3, the characteristic peaks at 14.11°, 28.41°, and 43.21° can be assigned to the (110), (220), and (330) planes of tetragonal CH$_3$NH$_3$PbI$_3$, respectively. The absence of the signature peak at 12.6° which corresponds to the (001) plane of PbI$_2$ indicates no decomposition of the bulk perovskite even after exposure to 200 cycles of ALD Al$_2$O$_3$.

From Figures 2 and 3 it can be concluded that the bulk changes which the perovskite material undergoes during the ALD process are negligible. To understand the effect of ALD Al$_2$O$_3$ on the perovskite surface, the differential IR spectra, which are defined by the difference in absorbance of the perovskite with and without Al$_2$O$_3$, are analyzed as a function of increasing number of ALD cycles (Figure 4a). In Figure 4a, the Al–O–Al phonon mode in the range of 1000–700 cm$^{-1}$ and the (OH)–Al=O stretching mode at 1080 cm$^{-1}$ appear already from 15 cycles, and are characteristics of the growth of ALD Al$_2$O$_3$. It is interesting to note that the shape of the detected Al–O–Al phonon mode on top of perovskite is different as compared to what has been reported earlier for ALD Al$_2$O$_3$ on top of Si. This might be indicative for a different growth behavior of ALD Al$_2$O$_3$ based on the underlying substrate. The peak at 1217 cm$^{-1}$ pertains to the Al–CH$_3$ species from unreacted TMA ligands. Meanwhile, the presence of negative N–H stretching vibrations (3132 and 3179 cm$^{-1}$) indicate abstraction of either NH$_3$ or CH$_3$NH$_2$ from the perovskite surface. This is corroborated by the complementary decrease in the N–H bending vibration at 1468 cm$^{-1}$. The absence of the asymmetric and symmetric O–H stretching modes of H$_2$O at 3500 and 3450 cm$^{-1}$, respectively, and the minor shift in the symmetric N–H stretching vibration with increasing Al$_2$O$_3$ cycles, again confirms that the interaction of H$_2$O molecule with the CH$_3$NH$_3^+$ of the perovskite is rather weak in our case. It is to be noted that the vibrational modes pertaining to the PbI$_3$ framework of the perovskite are not IR-active in the range of 4000–500 cm$^{-1}$ studied in this work. The vibrational modes related to H$_2$O (g) and CO$_2$ (g) originate from the residual gas phase species present in the ALD reactor, as well as from the fluctuations in the N$_2$-purged IR beam path. The integrated area of the negative N–H stretching modes is plotted as a function of ALD cycles in Figure 4b. As seen, the area decreases exponentially with respect to increasing number of ALD cycles, showing that the effusion of NH$_3$ or CH$_3$NH$_2$ species occur even after the deposition of 200 cycles of Al$_2$O$_3$. It is potentially related to a lower density of the ALD Al$_2$O$_3$ which is grown at a low deposition temperature of 80 °C, which allows for both out-diffusion of perovskite functional groups and in-diffusion of ALD precursors. To gain further insight into the chemical modifications in the perovskite surface as observed via IR, XPS analysis is carried out on the perovskite/ALD Al$_2$O$_3$ interface, for Al$_2$O$_3$ cycles ranging from 25 to 200. First, the growth of Al$_2$O$_3$ is witnessed by the presence of the characteristic Al 2p peak at 74.6 eV as shown in Figure S2 for a film obtained with 25 cycles. This corresponds to an Al$_2$O$_3$ thickness of <1 nm on top of perovskite, as was determined by measuring the attenuation of the iodine core level using eq 1 explained in the Experimental Section. Figure 5a presents the N 1s core level spectra for perovskite before and after deposition of 25 cycles of Al$_2$O$_3$. The binding energy (B.E.) peak at 402.7 eV which is representative of the N–C bonds present in the pristine perovskite decreases and shifts toward lower B.E. values. In addition, a new peak appears at a B.E. of 399.5 eV which is associated to primary or secondary amines. A similar behavior is observed in the C 1s spectra shown in Figure 5b where the disappearance of the characteristic C–N B.E. peak at 286.6 eV is well evident after deposition of 25 Al$_2$O$_3$ cycles. At the same time, the intensity of the C–C–H peak at 284.8 eV increases. This can be attributed to the formation
C–H bonds due to the deposition of ALD Al₂O₃ on top of the perovskite at a lower temperature of 80 °C. At the same time, the C–C/C–H area is also seen to increase after the deposition of ALD Al₂O₃ on top of Si substrate (SI Figure S3), confirming that it refers to carbon impurities in the Al₂O₃ layer. Meanwhile, monitoring the Pb 4f and I 3d spectra in Figure 5c and d, respectively, the formation of Pb–O (B.E. 137 eV) and I–O bonds (B.E. 624 eV) is not witnessed. This is indicative that the perovskite surface is not oxidized under the employed ALD conditions. In parallel, the reduction of Pb 4f and I 3d peak areas is well evident. A discussion on this will be presented later. It is interesting to note that even after 100 cycles of Al₂O₃ exposure (corresponding to a thickness of

Figure 5. Surface XPS spectra of (a) N₁s, (b) C₁s, (c) Pb₄f, and (d) I₃d peaks before and after deposition of 25 cycles of ALD Al₂O₃ (corresponding to <1 nm) on top of the perovskite film. Open circles, solid lines and dashed lines are measured data, peak fits, and cumulative fits, respectively.

Figure 6. Normalized integrated areas of (a) N₁s, Pb₄f, I₃d, and (b) Al₂p as a function of number of Al₂O₃ cycles on perovskite. The dashed lines show predictions assuming a layer-by-layer growth mechanism.
about 6.7 nm), the inorganic framework of the perovskite stays unoxidized, as shown in SI Figure S4.

The intensity of all perovskite elements is generally expected to decrease upon Al₂O₃ deposition because of the attenuation length, as predicted by eq 1. Figure 6a presents the normalized integrated areas of Pb 4f, I 3d, and N 1s elements as a function of number of ALD cycles. It is evident that integrated area of N 1s decreases significantly faster than the decays of Pb 4f and I 3d areas with increase in the number of Al₂O₃ cycles. Therefore, the reduced counts of the N−C peak (in Figure 5a) and the disappearance of the C−N peak (in Figure 5b) point out complete effusion of CH₃NH₂ from the perovskite surface. The consumption of the organic moiety as confirmed by XPS, is in agreement with the earlier drawn conclusion of CH₃NH₂ abstraction from IR analysis (Figure 4a). The dashed line in Figure 6a represents the expected exponential decay of the I 3d signal based on eq 1. It is interesting to note that the evolution of the integrated areas of I 3d and Al 2p as a function of number of Al₂O₃ cycles on perovskite (Figure 6a,b) is different when compared to the evolution of the integrated areas of Si 2p and Al 2p with increasing Al₂O₃ cycles on top of c-Si (SI Figure S5). This indicates different growth behavior of ALD Al₂O₃ based on the underlying substrate. We speculate that the growth of ALD Al₂O₃ on top of perovskite begins with island formation, followed by a transition to “layer-by-layer” deposition only after 75 ALD cycles. Recently, Kot et al. also demonstrated that the growth of ALD Al₂O₃ initiates in the form of small islands on perovskite. In addition, similar XPS results were obtained by Baker et al. for “island to layer-by-layer” growth behavior of ALD Pt on W adhesion layers.

In order to discern whether TMA or H₂O vapor is more deleterious to the perovskite, the drop in the intensities of the N−C B.E. peak with respect to individual TMA and H₂O vapor doses is presented in the N 1s spectra of Figure 7a and 7b, respectively. It is evident that TMA exposure on top of perovskite is more detrimental than H₂O vapor exposure in our employed ALD Al₂O₃ recipe. Similar conclusions are drawn when analyzing the C 1s spectra in SI Figure S6. Meanwhile, the I 3d counts experience no change irrespective of TMA and H₂O vapor doses (Figure 7c and d), again confirming the stability of the inorganic framework when exposed to the ALD precursor and co-reactant.

Surface −OH groups are considered to be the most common/ubiquitous chemisorption sites for TMA on Si substrates. In SI Figure S7, the absence of the characteristic OH B.E. peak in the O 1s spectrum of the pristine perovskite marks the absence of −OH surface groups in our employed CH₃NH₃PbI₃–ₓClₓ perovskite. Therefore, it is interesting to investigate how the growth of ALD Al₂O₃ initiates on top of the employed perovskite. Based on the obtained IR and XPS results, the proposed growth mechanism of ALD Al₂O₃ on top of CH₃NH₃PbI₃–ₓClₓ perovskite is schematically represented in Figure 8. During the first half-cycle, TMA reacts with the perovskite surface by interacting with the CH₃NH₃⁺ cation. This interaction weakens the hydrogen-bonds between CH₃NH₃⁺ and I⁻ of the perovskite, leading to breakdown of
the organic moiety from the inorganic framework. This is in accordance with the N 1s and C 1s XPS results (presented in Figure 7 and SI Figure S6) showing reduced counts of the N−C and C−N peaks, respectively upon TMA exposure. Alongside the release of CH₃NH₂ and CH₄ as byproducts, an adduct comprising of PbI₃−Al(CH₃)₂ is left behind. This PbI₃−Al(CH₃)₂ adduct can then react with the H₂O molecule during the subsequent half-cycle of H₂O dosage, and then generate the −OH surface sites necessary to promote the growth of Al₂O₃. The reaction mechanism proposed in this work via experimental investigation is in agreement with the one obtained from density functional theory (DFT) in the work of Choudhury et al.34

To study how the growth of ALD Al₂O₃ proceeds on top of perovskite and whether it follows the classical linear behavior which is observed typically on a c-Si substrate, the thicknesses of Al₂O₃ deposited on both perovskite and c-Si are calculated from XPS. Recently, Klesko et al. utilized a similar approach with XPS to calculate the thickness of ALD TiO₂ grown selectively on top of a Si substrate.66 The thickness of ALD Al₂O₃ is first inferred in the case of growth on c-Si and is presented in Figure 9a. As expected, the growth behavior of Al₂O₃ is linear with increasing ALD cycles. At the same time, it is well evident from Figure 9a that for all the ALD cycles, the thickness calculated from XPS is in good agreement with the thickness derived from SE, thus, validating the reliability of the XPS method for calculating the thickness of the grown ALD layer. Next, the growth behavior of ALD Al₂O₃ is monitored on top of the perovskite, and the calculated thicknesses from XPS are plotted as a function of the number of ALD cycles in Figure 9b. It is interesting to see that in case of perovskite, the growth of ALD Al₂O₃ is retarded during the first 75 cycles of deposition (corresponding thickness of about 5 nm). Only after 75 cycles, the growth catches up and follows the classical linear behavior. A cross-sectional TEM study is performed on the perovskite/ALD Al₂O₃ (200 cycles) interface as shown in Figure 9c, d. The thickness of Al₂O₃ determined from TEM is in agreement with the thickness calculated from XPS.

The reason for the growth delay of ALD Al₂O₃ on top of perovskite is not clear yet and requires further investigation. At present, we hypothesize that ALD Al₂O₃ grows initially in the form of small islands on top of perovskite, and only after 75 cycles (~5 nm Al₂O₃) conformal layer-by-layer growth starts to occur. The formation of a conformal ALD Al₂O₃ layer (after 200 cycles) on top of the perovskite surface is well evident in the EDX elemental mapping acquired using TEM (Figure 9e). Similar behavior was demonstrated recently by Kot et al., where ALD Al₂O₃ was shown to grow initially in the form of small islands on top of perovskite.23 At the same time, following the proposed mechanism in this work (Figure 8),

Figure 9. (a) Thickness of ALD Al₂O₃ on top of Si with increasing number of ALD cycles derived from XPS and SE (b) Thickness of ALD Al₂O₃ on top of perovskite as a function of number of ALD cycles. The dashed line is a linear fit. The thickness calculation was repeated for three batches to calculate the standard deviation, and thereby the respective error bars. (c), (d) High angle annular dark field (HAADF) scanning TEM cross-sectional images of 200 cycles (14 ± 1 nm) ALD Al₂O₃ deposited on top of the perovskite film taken at different resolutions. (e) Corresponding overlapping EDX elemental mapping image.
one might expect the growth of $\text{Al}_2\text{O}_3$ on perovskite to accelerate only after exposure to certain number of ALD cycles, possibly, when the organic cation is sufficiently eliminated from the perovskite surface by adequate TMA exposure, which could then lead to the availability of sufficient $-\text{OH}$ surface sites necessary to promote the linear growth behavior of $\text{Al}_2\text{O}_3$.

### CONCLUSIONS

In summary, the bulk and surface chemical modifications in the $\text{CH}_3\text{NH}_3\text{PbI}_3-\text{Cl}$ perovskite upon growth of ALD $\text{Al}_2\text{O}_3$ have been investigated by combining in situ IR spectroscopy and ex situ XPS analysis. The ALD precursors do not diffuse into the bulk of the perovskite. However, with increasing number of ALD $\text{Al}_2\text{O}_3$ cycles, abstraction of $\text{NH}_3$ or $\text{CH}_3\text{NH}_2$ from the perovskite surface is witnessed. Meanwhile, XPS analysis confirms the diffusion of $\text{CH}_3\text{NH}_2$ from the perovskite surface, with no oxidation of the inorganic framework. In addition, TMA doses on top of perovskite are found to be more detrimental than $\text{H}_2\text{O}$ doses in our employed ALD $\text{Al}_2\text{O}_3$ recipe. A plausible growth mechanism of ALD $\text{Al}_2\text{O}_3$ on top of perovskite is discussed, where TMA reacts with the perovskite surface by interacting with the $\text{CH}_3\text{NH}_2^+$ cation. This reaction releases $\text{CH}_3\text{NH}_2$ and $\text{CH}_2$ as byproducts, and leaves behind an aduct comprising of $\text{PbI}_2-\text{Al}(\text{CH}_3)_2$ to react with the $\text{H}_2\text{O}$ molecule during the subsequent half-cycle of $\text{H}_2\text{O}$ dosage, and generate the $-\text{OH}$ surface sites necessary to promote the growth of $\text{Al}_2\text{O}_3$. An attenuated growth of $\text{Al}_2\text{O}_3$ is observed on top of perovskite during the first 75 cycles ($\sim$5 nm) of exposure, and, only thereafter, it follows the classical linear behavior that is conventionally seen on top of c-Si substrate. We believe that the insights achieved by in situ IR and XPS studies in this work will contribute to the advancement in engineering of ALD metal oxides directly on perovskite.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b18307.

Schematic illustration of the approach followed for calculating the absorbance on perovskite, XPS survey spectra together with additional surface spectra of $\text{Al}_2\text{p}$, $\text{N}$ 1$s$, $\text{Pb}$ 4$f$, and $\text{I}$ 3$d$ peaks before and after deposition of different cycles of ALD $\text{Al}_2\text{O}_3$ on top of the perovskite film, $\text{C}$ 1$s$ and O 1$s$ spectra measured for the perovskite film before and after 200 $\text{H}_2\text{O}$ vapor doses, N 1$s$, C 1$s$ and I 3$d$ peaks of the perovskite film before and after exposure to 80 °C for 5 h inside the ALD chamber (at 10$^{-9}$ mbar), integrated areas of $\text{Si}$ 2$p$ and $\text{Al}$ 2$p$ as a function of number of ALD $\text{Al}_2\text{O}_3$ cycles on top of c-Si substrate, change in the N–H stretching mode of the perovskite after exposure to 80 °C for 5 h inside the ALD chamber (at 10$^{-9}$ mbar), change in the N–H stretching mode of the perovskite upon continuous exposure to 200 $\text{H}_2\text{O}$ vapor doses, additional EDX elemental mapping images of elements in the perovskite/ALD $\text{Al}_2\text{O}_3$/Spiro-OMeTAD sample (PDF)

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### Notes

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