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

Citation for published version (APA):
Koushik, D., Hazendonk, L., Zardetto, V., Vandalon, V., Verheijen, M. A., Kessels, W. M. M., & Creatore, M. (2019). Chemical analysis of the interface between hybrid organic–inorganic perovskite and atomic layer deposited Al2O3. ACS Applied Materials & Interfaces, 11(5), 5526-5535. https://doi.org/10.1021/acsami.8b18307

Document license:
CC BY-NC-ND

DOI:
10.1021/acsami.8b18307

Document status and date:
Published: 06/02/2019

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Chemical Analysis of the Interface between Hybrid Organic–Inorganic Perovskite and Atomic Layer Deposited Al2O3

Dibyashree Koushik, Lotte Hazendonk, Valerio Zardetto, Vincent Vandalon, Marcel A. Verheijen, Wilhelmus M.M. Kessels, and Mariadriana Creatore

Department of Applied Physics, Eindhoven University of Technology (TU/e), P.O. Box 513, S600 MB Eindhoven, The Netherlands

Solliance, High Tech Campus 21, 5656 AE Eindhoven, The Netherlands

Philips Innovation Labs, High Tech Campus 11, 5656 AE Eindhoven, The Netherlands

Supporting Information

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–Cl 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–Cl 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 CH3NH3 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.1 However, the presence of the volatile CH3NH3+ component in its lattice structure makes this perovskite highly unstable against environmental exposure.2–5

Massive efforts have been made to enhance the environmental stability of the perovskite solar cells (PSCs)6 by focusing on more stable perovskite compositions7–9 and/or adopting the approach of interface engineering.10–16 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.17–25 The work reported from our group showed that the implementation of ultrathin thermal ALD Al2O3 (<1 nm) directly on top of CH3NH3PbI3–Cl 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).22

Received: October 19, 2018
Accepted: January 9, 2019
Published: January 9, 2019
Kot et al. demonstrated the incorporation of room-temperature ALD Al$_2$O$_3$ on top of both fresh$^{23}$ and 50 days aged$^{24}$ CH$_3$NH$_3$PbI$_3$ perovskite to improve the power conversion efficiency (PCE) of the PSC and its ambient air stability. The applicability of ALD Al$_2$O$_3$ was extended also toward other perovskite chemistries in the work of Louidice et al., where an ALD Al$_2$O$_3$ layer was adopted to stabilize CsPbBr$_3$Cl$_x$ and CsPbI$_3$ quantum dots. In contrast to the above ALD Al$_2$O$_3$ processes which used trimethylaluminum (TMA) and H$_2$O vapor as the precursor and co-reactant respectively, Kim et al. utilized aluminum triisopropoxide and acetic acid in view of a water-free ALD Al$_2$O$_3$ process to passivate CH$_3$NH$_3$PbI$_3$ 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 Al$_2$O$_3$ effects directly on top of perovskites, the application of ALD has expanded further toward other metal oxides, among which metal (XRD) and XPS were utilized to demonstrate the role of bulk and surface stability of the perovskite during ALD.$^{17,33,37}$

In this work, we perform in situ IR spectroscopy on CH$_3$NH$_3$PbI$_3$Cl$_x$ perovskite to study its structural and chemical modifications during the growth of ALD Al$_2$O$_3$ on top, employing TMA as the precursor and H$_2$O vapor as the co-reactant at 80 °C. We choose ALD Al$_2$O$_3$ 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 Al$_2$O$_3$ interface. Based on the XPS results, we discuss how the growth of ALD Al$_2$O$_3$ can initiate and then further develop on top of CH$_3$NH$_3$PbI$_{3−x}$Cl$_x$ perovskite.

**EXPERIMENTAL SECTION**

**CH$_3$NH$_3$PbI$_3$Cl$_x$ Perovskite Film Preparation.** The perovskite precursor solution is made by mixing lead acetate (PbAc$_2$), lead chloride (PbCl$_2$) 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 N$_2$ 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 Al$_2$O$_3.$** Al$_2$O$_3$ 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 H$_2$O vapor dose of 0.1 s, followed by a purge of 4.0 s. The thickness of the ALD Al$_2$O$_3$ 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 ∼10 000−50 000 cm$^{-1}$). The substrate is mounted onto a sample manipulator (PREVAC, four axes manipulator), which enables for a well-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 N$_2$ 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 N$_2$ 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 before 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 (I$_0$/I$_1$), where I$_0$ and I$_1$ are the measured transmittance of the sample after and before Al$_2$O$_3$ 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 Al$_2$O$_3$/perovskite/Si samples using a PANalytical X'Pert Pro MRD X-ray diffractometer using Cu K$_{α}$ radiation ($λ = 1.540598$ A) in the 2$θ$ range 10−60° at a scanning rate of 1.5° min$^{-1}$. XPS. Ex situ XPS measurements are carried out right after the ALD Al$_2$O$_3$ deposition on perovskite. The perovskite/ALD Al$_2$O$_3$ samples are transferred to the XPS setup in N$_2$ 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 ($K_{\alpha}$, 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 Advantage software applying Powell fitting algorithm and Gauss-Lorentz Mix. The Al$_2$O$_3$ film thickness on top of the Si substrate ($d_{\text{Al2O3}}$) is calculated by measuring the attenuation of the silicon core level using eq 1, which is given as,

$$I_s = I_o \exp \left[ - \frac{d_{\text{Al2O3}}}{\lambda_{\text{IMFP}} \sin \theta} \right]$$  \hspace{1cm} (1)

where, $I_s$ is the photoelectron yield with Al$_2$O$_3$ on Si, $I_o$ is the photoelectron yield without Al$_2$O$_3$ on Si, $d$ is the Al$_2$O$_3$ 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.

Similar procedure is utilized to calculate the thickness of ALD Al$_2$O$_3$ on top of perovskite, by measuring the attenuation of the iodine core level using eq 1. The photoelectron yields $I_s$ and $I_o$ are obtained by integrating the area under the I 3d peaks before and after Al$_2$O$_3$ deposition, respectively. The IMFP of electron is taken to be 2.63 nm for Al$_2$O$_3$. The XPS takeoff angle is 90°. It should be noted that the value of $\lambda_{\text{IMFP}}$ 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 Al$_2$O$_3$/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 mm$^2$ 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 CH$_3$NH$_3$PbI$_3$-xCl$_x$ perovskite film. The observed vibrational modes (summarized in Table 1) are in good agreement with those reported in literature. The most intense vibrational mode is marked by the symmetric and asymmetric N–H stretching modes (associated with NH$_3^+$) 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 NH$_3^+$ stretching modes of the perovskite undergoes during consecutive cycles of ALD Al$_2$O$_3$. A decrease in both symmetric (3132 cm$^{-1}$) and asymmetric (3179 cm$^{-1}$) N–H stretching modes is evident upon increasing the number of Al$_2$O$_3$ cycles. At the same time, narrowing of the NH$_3^+$ 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 CH$_3$NH$_3^+$ 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%. 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 H$_2$O) indicating that diffusion of water molecules does not occur into the bulk of the perovskite. In the employed ALD Al$_2$O$_3$ recipe, the perovskite is exposed to consecutive H$_2$O pulses of 1×10$^5$ L which results in a significantly lower R.H. environment (maximum of 0.1%) in the ALD chamber. Hence, the interaction between H$_2$O molecule and CH$_3$NH$_3^+$ is rather weak during our H$_2$O dosage step. This is in agreement with Li et al., where it was shown that H$_2$O exposure of below 2×10$^5$ L does cause degradation of CH$_3$NH$_3$PbI$_3$. The IR results indicating negligible bulk decomposition of the perovskite are also

![Table 1. Characteristic IR-Active Vibrational Modes of the Pristine CH$_3$NH$_3$PbI$_3$-xCl$_x$ Perovskite](image)

| Wavenumber (cm$^{-1}$) | Vibrational Mode |
|------------------------|-----------------|
| 3179                   | N–H stretch (asymmetric) |
| 3132                   | N–H stretch (symmetric) |
| 2958                   | C–H stretch (asymmetric) |
| 2921                   | C–H stretch (symmetric) |
| 1577                   | N–H bend (asymmetric) |
| 1469                   | N–H bend (symmetric) |
| 1249, 910              | CH$_3$NH$_3^+$ rock |
| 962                    | C–N stretch |
| 2817, 2711, 2488, 2375, 1840 | CH$_3$NH$_3^+$ resonant |

![Figure 2. Change in the N–H stretching mode of the ~300 nm thick perovskite upon continuous exposure to cycles of ALD Al$_2$O$_3$.](image)
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 CH₃NH₃PbI₃, respectively. The absence of the signature peak at 12.6° which corresponds to the (001) plane of PbI₂ indicates no decomposition of the bulk perovskite even after exposure to 200 cycles of ALD Al₂O₃.

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 Al₂O₃ on the perovskite surface, the differential IR spectra, which are defined by the difference in absorbance of the perovskite with and without Al₂O₃, 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 Al₂O₃. 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 Al₂O₃ on top of Si. This might be indicative for a different growth behavior of ALD Al₂O₃ based on the underlying substrate. The peak at 1217 cm⁻¹ pertains to the Al−CH₃ species from unreacted TMA ligands. Meanwhile, the presence of negative N−H stretching vibrations (3132 and 3179 cm⁻¹) indicate abstraction of either NH₃ or CH₃NH₂ 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 H₂O at 3500 and 3450 cm⁻¹, respectively, and the minor shift in the symmetric N−H stretching vibration with increasing Al₂O₃ cycles, again confirms that the interaction of H₂O molecule with the CH₃NH₃⁺ of the perovskite is rather weak in our case. It is to be noted that the vibrational modes pertaining to the PbI₂ 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 H₂O (g) and CO₂ (g) originate from the residual gas phase species present in the ALD reactor, as well as from the fluctuations in the N₂/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 NH₃ or CH₃NH₂ species occur even after the deposition of 200 cycles of Al₂O₃. It is potentially related to a lower density of the ALD Al₂O₃ 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 Al₂O₃ interface, for Al₂O₃ cycles ranging from 25 to 200. First, the growth of Al₂O₃ is witnessed by the presence of the characteristic Al 2p peak at 74.6 eV as shown in SI Figure S2 for a film obtained with 25 Al₂O₃ cycles. This corresponds to an Al₂O₃ 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 Al₂O₃. The binding energy (B.E.) peak at 402.7 eV as shown in SI Figure S2 is a representative of the N−H stretching mode, which is negative compared to the baseline, increases in magnitude with increasing number of ALD cycles. The dashed line is a fit to the exponential function exp(-rx), where, x = number of Al₂O₃ cycles and r = effusion rate of NH₃ or CH₃NH₂ species per cycle.
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),...
one might expect the growth of Al₂O₃ 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 –OH surface sites necessary to promote the linear growth behavior of Al₂O₃.

## CONCLUSIONS

In summary, the bulk and surface chemical modifications in the CH₃NH₃PbI₃₋ₓClₓ perovskite upon growth of ALD Al₂O₃ have been investigated by combining in situ IR spectroscopy study and ex situ XPS analysis. The ALD precursors do not diffuse into the bulk of the perovskite. However, with increasing number of ALD Al₂O₃ cycles, abstraction of NH₃ or CH₃NH₃ from the perovskite surface is witnessed. Meanwhile, XPS analysis confirms the effusion of CH₃NH₃ from the perovskite surface, with no oxidation of the inorganic byproducts, and leaves behind an adduct comprising of PbI₃⁻ cation. This reaction releases CH₂NH₂ and CH₃ as byproducts, and leaves behind an adduct comprising of PbI₃⁻⁻⁻ Al(CH₃)₃ to react with the H₂O molecule during the subsequent half-cycle of H₂O dosage, and generate the –OH surface sites necessary to promote the growth of Al₂O₃. An attenuated growth of Al₂O₃ is observed on top of perovskite during the first 75 cycles (~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 Al 2p, N 1s, Pb 4f, and I 3d peaks before and after deposition of different cycles of ALD Al₂O₃ on top of the perovskite film, C 1s and O 1s spectra measured for the perovskite film before and after 200 H₂O vapor doses, N 1s, C 1s and I 3d peaks of the perovskite film before and after 48 h of exposure to vacuum conditions (10⁻⁹ mbar), integrated areas of Si 2p and Al 2p as a function of number of ALD Al₂O₃ 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 10⁻⁸ mbar), change in the N−H stretching mode of the perovskite upon continuous exposure to 200 H₂O vapor doses, additional EDX elemental mapping images of elements in the perovskite/ALD Al₂O₃/Spiro-OMeTAD sample (PDF)

## ORCID

Dibyashree Koushik: 0000-0002-7609-3544
Wilhelmus M.M. Kessels: 0000-0002-7630-8226

## REFERENCES

1. NREL. Best Research-Cell Efficiencies [http://www.nrel.gov/ncpv/images/efficiency_chart.jpg](http://www.nrel.gov/ncpv/images/efficiency_chart.jpg) (accessed September 13, 2018).
2. Ze, W.; Zejiao, S.; Taotao, L.; Yonghua, C.; Wei, H. Stability of Perovskite Solar Cells: A Prospective on the Substitution of the A Cation and X Anion. Angew. Chem., Int. Ed. 2017, 56 (S), 1190–1212.
3. Wang, D.; Wright, M.; Elumalai, N. K.; Uddin, A. Stability of Perovskite Solar Cells. Sol. Energy Mater. Sol. Cells 2016, 147, 255–275.
4. Niu, G.; Guo, X.; Wang, L. Review of Recent Progress in Chemical Stability of Perovskite Solar Cells. J. Mater. Chem. A 2015, 3 (17), 8970–8980.
5. Conings, B.; Drijkoningen, J.; Gauquelin, N.; Babayigit, A.; D’Haen, J.; D’Oliealaeger, L.; Ethirajan, A.; Verbeeck, J.; Manca, J.; Mosconi, E.; Angelis, F. D.; Boyen, H.-G. Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite. Adv. Energy Mater. 2015, 5 (15), 1500477.
6. Fu, X.; Tang, X.; Huang, B.; Hu, T.; Tan, L.; Chen, L.; Chen, Y. Recent Progress on the Long-Term Stability of Perovskite Solar Cells. Adv. Science 2018, 5 (S), 1700387.
7. Saliba, M.; Matsu, T.; Domanski, K.; Seo, J.-Y.; Ummdasingu, A.; Zakeeruddin, S. M.; Correa-Baena, J.-P.; Tress, W. R.; Abate, A.; Hagfeldt, A.; Grätzel, M. Incorporation of Rubidium Cations into Perovskite Solar Cells Improves Photovoltaic Performance. Science 2016, 354 (6309), 206–209.
8. Saliba, M.; Matsu, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Grätzel, M. Cesium-Containing Triple Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency. Energy Environ. Sci. 2016, 9 (6), 1989–1997.
9. Li, Y.; Ji, L.; Liu, R.; Zhang, C.; Mak, C. H.; Zou, X.; Shen, H.-H.; Leu, S.-Y.; Hsu, H.-Y. A Review on Morphology Engineering for Highly Efficient and Stable Hybrid Perovskite Solar Cells. J. Mater. Chem. A 2018, 6 (27), 12842–12875.
10. Bai, Y.; Meng, X.; Yang, S. Interface Engineering for Highly Efficient and Stable Planar p-i-n Perovskite Solar Cells. Adv. Energy Mater. 2018, 8 (5), 1701883.
11. Lira-Cantú, M. Perovskite Solar Cells: Stability Lies at Interfaces. Nat. Energy 2017, 2, 17115.
12. Fakhruddin, A.; Schmidt-Mende, L.; Garcia-Belmonte, G.; Jose, R.; Mora-Sero, I. Interfaces in Perovskite Solar Cells. Adv. Energy Mater. 2017, 7 (22), 1700623.
13. Christians, J. A.; Schulz, P.; Tinkham, J. S.; Schloemer, T. H.; Harvey, S. P.; Tremolet de Villers, B. J.; Sellinger, A.; Berry, J. J.; Luther, J. M. Tailored Interfaces of Unencapsulated Perovskite Solar
Cells for >1,000 h Operational Stability. Nat. Energy 2018, 3 (1), 68–74.

(14) Hou, Y.; Du, X.; Scheiner, S.; McMeekin, D. P.; Wang, Z.; Li, N.; Killian, M. S.; Chen, H.; Richter, M.; Levchuk, I.; Schrenker, N.; Speicker, E.; Stubhan, T.; Luechinger, N. A.; Hirsch, A.; Schmuki, P.; Steinrück, H.-P.; Pink, R. H.; Malik, M.; Snith, H. J.; Brabec, C. J. A Generic Interface to Reduce the Efficiency-Stability-Cost Gap of Perovskite Solar Cells. Science 2017, 358 (6367), 1192–1197.

(15) Rajappal, A.; Yao, K.; Jen, A. K.-Y. Toward Perovskite Solar Cell Commercialization: A Perspective and Research Roadmap Based on Interfacial Engineering. Adv. Mater. 2018, 30, 1800455.

(16) Pérez-del-Rey, D.; Boix, P. P.; Sessolo, M.; Hadiopour, A.; Bolink, H. J. Interfacial Modification for High-Efficiency Vapor-Phase-Deposited Perovskite Solar Cells Based on a Metal Oxide Buffer Layer. J. Phys. Chem. Lett. 2018, 9 (5), 1041–1046.

(17) Zardetto, V.; Williams, B. L.; Perrotta, A.; Di Giacomo, F.; Verheijen, M. A.; Andriessen, R.; Kessels, W. M. M.; Creatore, M. Atomic Layer Deposition for Perovskite Solar Cells: Research Status, Opportunities and Challenges. Sustain. Energy Fuels 2017, 1 (1), 30–55.

(18) Deng, K.; Li, L. Advances in the Application of Atomic Layer Deposition for Organic-Metal Halide Perovskite Solar Cells. Adv. Mater. Interfaces 2016, 3 (21), 1600505.

(19) Choi, E. Y.; Kim, J.; Lim, S.; Han, E.; Ho-Baillie, A. W. Y.; Park, N. Enhancing Stability for Organic-Inorganic Perovskite Solar Cells by Atomic Layer Deposited Al2O3 Encapsulation. Sol. Energy Mater. Sol. Cells 2018, 188, 37–45.

(20) Ramos, F. J.; Maindron, T.; Béchu, S.; Rebai, A.; Frégnaux, M.; Bouttemy, M.; Rousset, J.; Schulz, P.; Schneider, N. Versatile Perovskite Solar Cell Encapsulation by Low-Temperature ALD-Al2O3 with Long-Term Stability Improvement. Sustain. Energy Fuels 2018, 2, 2468–2479.

(21) Dong, X.; Fang, X.; Lv, M.; Lin, B.; Zhang, S.; Ding, J.; Yuan, N. Improvement of the Humidity Stability of Organic–Inorganic Perovskite Solar Cells Using Ultrathin Al2O3 Layers Prepared by Atomic Layer Deposition. J. Mater. Chem. A 2015, 3 (10), 5360–5367.

(22) Koushik, D.; Verhees, W. J. H.; Kuang, Y.; Veenstra, S.; Zhang, D.; Verheijen, M. A.; Creatore, M.; Schropp, R. E. I. High-Efficiency Humidity-Stable Planar Perovskite Solar Cells Based on Atomic Layer Architecture. Energy Environ. Sci. 2017, 10 (1), 91–100.

(23) Kot, M.; Kegelein, L.; Das, C.; Kus, P.; Tsud, N.; Matolinova, I.; Albrecht, S.; Matolin, V.; Schmeisser, D. Room Temperature Atomic Layer Deposited Al2O3 Improves Perovskite Solar Cells Efficiency Over Time. ChemSusChem 2018, 11, 3640.

(24) Kot, M.; Das, C.; Wang, Z.; Henkel, K.; Rouissi, Z.; Wojciechowski, K.; Snith, H. J.; Schmeisser, D. Room-Temperature Atomic Layer Deposition of Al2O3 on CH3NH3PbI3, Characterized by Synchrotron-Based X-Ray Photoelectron Spectroscopy. Inorg. Molecules Phys. Res., Sect. B 2017, 411, 49–52.

(25) Hultqvist, A.; Aitola, K.; Svinbjörnsen, K.; Säki, Z.; Larsson, F.; Törndahl, T.; Johansson, E.; Boschloo, G.; Edoff, M. Atomic Layer Deposition of Electron Selective SnOx and ZnO Films on Mixed Halide Perovskite: Compatibility and Performance. ACS Appl. Interfaces 2018, 10 (4), 28948–28954.

(26) Qi, P.; Mercx, T.; Jaysankar, M.; Masse de la Huerta, C.; Rakocvic, L.; Zhang, W.; Paetzold, U. W.; Gehlhaar, R.; Froyen, L.; Poortmans, J.; Cheyns, D.; Snith, H. J.; Heremans, P. Pinhole-Free Perovskite Films for Efficient Solar Modules. Energy Environ. Sci. 2016, 9 (2), 484–489.

(27) Heil, S. B. S.; Landereis, E.; Roezenboom, F.; van de Sanden, M. C. M.; Kessels, W. M. M. Low-Temperature Deposition of TiOx by Plasma-Assisted Atomic Layer Deposition. J. Electrochem. Soc. 2006, 153 (11), G956–G965.

(28) Bellanato, J. Infra-Red Spectra of Ethylenediamine Dihydrochloride and Other Amine Hydrochlorides in Alkali Halide Disks. J. Phys. Chem. A 1960, 63 (1), 1344–1357.

(29) Kim, I. S.; Cao, D. H.; Buchholz, D. B.; Emery, J. D.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G.; Martinson, A. B. F. Liquid Water- and Heat-Resistant Hybrid Perovskite Photovoltaics via An Inverted ALD Oxide Electron Extraction Layer Design. Nano Lett. 2016, 16 (12), 7786–7790.
and Low-Temperature Infrared Spectra. *J. Phys. Chem. C* **2015**, *119*(46), 25703–25718.

(45) Müller, C.; Glaser, T.; Plogmeyer, M.; Sendner, M.; Döring, S.; Bakulin, A. A.; Brzuska, C.; Scheer, R.; Pshenichnikov, M. S.; Kowalsky, W.; Pucci, A.; Lovrinčić, R. Water Infiltration in Methylammonium Lead Iodide Perovskite: Fast and Inconspicuous. *Chem. Mater.* **2015**, *27*(22), 7835–7841.

(46) Halder, A.; Choudhury, D.; Ghosh, S.; Subbiah, A. S.; Sarkar, S. K. Exploring Thermochromic Behavior of Hydrated Hybrid Perovskites in Solar Cells. *J. Phys. Chem. Lett.* **2015**, *6*(16), 3180–3184.

(47) Zhu, Z.; Hadjiiev, V. G.; Rong, Y.; Guo, R.; Cao, B.; Tang, Z.; Qin, F.; Li, Y.; Wang, Y.; Hao, F.; Venkatesan, S.; Li, W.; Baldelli, S.; Golyu, A. M.; Fang, H.; Hu, Y.; Yao, Y.; Wang, Z.; Bao, J. Interaction of Organic Cation with Water Molecule in Perovskite MAPbI3: From Dynamic Orientational Disorder to Hydrogen Bonding. *Chem. Mater.* **2016**, *28*(20), 7385–7393.

(48) Li, Y.; Xu, X.; Wang, C.; Wang, C.; Xie, F.; Yang, J.; Gao, Y. Degradation by Exposure of Coevaporated CH3NH3PbI3 Thin Films. *J. Phys. Chem. C* **2015**, *119*(42), 23996–24002.

(49) Frank, M. M.; Chabal, Y. J.; Green, M. L.; Delabie, A.; Brijs, B.; Wilk, G. D.; Ho, M.-Y.; Rosa, E. B. O. d.; Baumöl, I. J. R.; Stedile, F. C. Enhanced Initial Growth of Atomic-Layer-Deposited Metal Oxides on Hydrogen-Terminated Silicon. * Appl. Phys. Lett.* **2003**, *83*(4), 740–742.

(50) Frank, M. M.; Chabal, Y. J.; Wilk, G. D. Nucleation and Interface Formation Mechanisms in Atomic Layer Deposition of Gate Oxides. *Appl. Phys. Lett.* **2003**, *82*(26), 4758–4760.

(51) Fan, G.; Wang, Y.; Wang, C. One-Pot Synthesis of Aluminum Oxyhydroxide Matrix-Entrapped Pt Nanoparticles as an Excellent Catalyst for the Hydrogenation of Nitrobenezene. *RSC Adv.* **2014**, *4*(21), 10997–11002.

(52) Shen, S. C.; Chen, Q.; Chow, P. S.; Tan, G. H.; Zeng, X. T.; Wang, Z.; Tan, R. B. H. Steam-Assisted Solid Wet-Gel Synthesis of High-Quality Nanorods of Boehmite and Alumina. *J. Phys. Chem. C* **2007**, *111*(2), 700–707.

(53) Vazhayal, L.; Kumar Sasidharan, N.; Talasila, S.; Kumar, D. B. S.; Solaiappan, A. Supramolecular Association of 2D Alumino-Siloxane Aquagel Building Blocks to 3D Porous Cages and its Efficacy for Topical and Injectable Delivery of Fluconazole, An Antifungal Drug. *J. Mater. Chem. B* **2015**, *3*(29), 5978–5990.

(54) Levrau, E.; Van de Kerckhove, K.; Devloo-Casier, K.; Pulinthanthu Sree, S.; Martens, J. A.; Detavernier, C.; Dendooven, J. In Situ IR Spectroscopic Investigation of Alumina ALD on Porous Silicon Films: Thermal versus Plasma-Enhanced ALD. *J. Phys. Chem. C* **2014**, *118*(31), 29854–29859.

(55) Bartram, M. E.; Michalske, T. A.; Rogers, J. W. A Reexamination of the Chemisorption of Trimethylaluminum on Silica. *J. Phys. Chem.* **1991**, *95*(11), 4453–4463.

(56) Dillon, A. C.; Ott, A. W.; Way, J. D.; George, S. M. Surface Chemistry of Al2O3 Deposition Using Al(CH3)3 and H2O in a Binary Reaction Sequence. *Surf. Sci.* **1995**, *322*(1), 230–242.

(57) Goldstein, D. N.; McCormick, J. A.; George, S. M. Al2O3 Atomic Layer Deposition with Trimethylaluminum and Ozone Studied by in Situ Transmission FTIR Spectroscopy and Quadrupole Mass Spectrometry. *J. Phys. Chem. C* **2008**, *112*(49), 19530–19539.

(58) Idigoras, J.; Todiño, A.; Sanchez-Valencia, J. R.; Barranco, A.; Borras, A.; Anta, J. A. The Interaction Between Hybrid Organic-Inorganic Halide Perovskite and Selective Contacts in Perovskite Solar Cells: An Infrared Spectroscopy Study. *Phys. Chem. Chem. Phys.* **2016**, *18*(19), 13583–13590.

(59) Bosch, R. H.; Coudow, C.; Cornelissen, L. E.; Knoops, H. C. M.; Kessels, W. M. M. Atomic Layer Deposition of Silicon Nitride from Bis(tertiary-butyl-amino)silane and N2 Plasma Studied by in Situ Gas Phase and Surface Infrared Spectroscopy. *Chem. Mater.* **2016**, *28*(16), 5864–5871.

(60) Dingemans, G.; Kessels, W. M. M. Status and Prospects of Al2O3-Based Surface Passivation Schemes for Silicon Solar Cells. *J. Vac. Sci. Technol., A* **2012**, *30*(4), 040802.