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On the effect of atomic layer deposited Al_2O_3 on the environmental degradation of hybrid perovskite probed by positron annihilation spectroscopy†

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The degradation of hybrid perovskite films when exposed to ambient air is a major challenge for the development of perovskite-based photovoltaics at large scale. At present, little is known about the environmental degradation of perovskite films associated with the development of structural defects or open volumes (such as atomic vacancies, voids, crystallographic defects and grain boundary defects) in the lattice, and about the depth dependence of the structural degradation. Therefore, in this work, we use Doppler broadening-positron annihilation spectroscopy (DB-PAS) depth-profiling to gain insight into the structural degradation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite when exposed to ambient air. In parallel, we investigate the effect of ultrathin (<1 nm) atomic layer deposited (ALD) Al_2O_3 processed directly on top of the perovskite as a means to suppress the degradation process. Specifically, we infer that the perovskite degradation involves changes in open volumes in its crystal lattice. This could be caused by the ingress of H_2O molecules into the cation vacancies. In parallel, chemical changes in the perovskite films upon decomposition are observed, accompanied by a decrease in the film thickness as a function of air exposure time. When the perovskite films are decorated with ALD Al_2O_3 , the latter delays the thickness reduction of the perovskite layer during air exposure and also suppresses the changes in its open volumes and chemical transformations. Our findings illustrate that an improved understanding of the perovskite degradation process can be obtained using DB-PAS, especially when combined with other thin film characterization techniques, such as X-ray diffraction and X-ray photoelectron spectroscopy.

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Introduction

The impressive power conversion efficiencies (PCEs) achieved over the past years¹ have placed the hybrid perovskite technology at the forefront of photovoltaic (PV) research. Organo-metal halide

perovskites possess unique attributes, such as tunable bandgap, high absorption coefficient, steep absorption edge and long charge carrier diffusion length.^{2–5} Methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) perovskite has been extensively implemented as a photo-absorber layer to yield high-efficiency solar cells. However, despite the remarkable initial performance, the material gradually decomposes into PbI_2 over time when exposed to ambient air because of the interaction with infiltrating water and oxygen molecules.^{6,7} To suppress or limit its degradation, notable efforts have been made either to synthesize stable perovskite chemical compositions,^{8,9} and/or engineer interfaces between the passivation, charge transport, and perovskite layers in the solar cell architectures.^{10–13}

In the case of interface engineering, the implementation of atomic layer deposited (ALD) metal oxides in perovskite device architectures has been proven to be one of the successful strategies in enhancing its environmental stability.^{14,15} Our previous work showed that ALD Al_2O_3 (<1 nm) deposited directly on top of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite^{16,17} prolongs

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† Electronic supplementary information (ESI) available: XPS spectrum of the $\text{Al}2p$ peak of perovskite/ALD Al_2O_3 film at day 0, DB-PAS depth-profiles of S - and W -parameters of the TiO_2/ITO film, and the perovskite/ALD Al_2O_3 (15 cycles) film at day 0 and after 3, 6, 12 and 22 days of air exposure, cross-sectional SEM images of the investigated layer stacks at day 0 and day 22. See DOI: 10.1039/c8tc06330c

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the humidity-stability of the solar cells for over 60 days in comparison to the Al_2O_3 -free cell (when exposed to a relative humidity of 40–70% at room temperature).¹⁶ Kim *et al.* demonstrated the implementation of ALD Al_2O_3 to stabilize $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films under a relative humidity of 85% for over 210 hours.¹⁸ Kot *et al.* incorporated room-temperature ALD Al_2O_3 on top of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite to improve both the power conversion efficiency (PCE) and the ambient air stability of the devices for 355 days.^{19,20} In the meantime, other ALD metal oxides (such as, TiO_2 ,²¹ SnO_2 ,^{22–24} ZrO_2 ,²⁵ Al-doped ZnO ²⁶) in combination with a [6,6]-Phenyl-C61 butyric acid methyl ester (PCBM) layer have been demonstrated to provide excellent moisture and thermal-stress stability to the perovskite solar cells (PSCs).

Despite these impressive advancements, the degradation process of hybrid perovskites in general, and the enhanced stability of the perovskite films when decorated with ultrathin ALD metal oxides (in particular, Al_2O_3) is not fully understood yet. Techniques such as X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) have been commonly employed to extract information on the bulk perovskite (in terms of change in crystal structure) or on its surface (in terms of change in chemical bonding), respectively. However, these techniques are not suited to gain understanding on the structural defects (open volumes) that are present in the hybrid organic–inorganic perovskite materials, such as crystallographic defects, grain boundary defects, voids, ionic defects (methylammonium, iodine and lead vacancies),^{27–34} when the perovskite films are exposed to the ambient environment. In addition, little is known about how the degradation evolves as a function of depth within the perovskite layer. It has been clearly demonstrated by experimental and theoretical studies that structural defects can promote the ingress of oxygen or moisture, leading to the degradation of the perovskite films and the solar cells.^{31–33} Thus, it is relevant to investigate whether the presence of ALD metal oxides on top of the perovskite is helpful in suppressing the evolution of the structural defects (or open volumes) in the perovskite lattice under exposure to the ambient environment.

To address this matter, we employ Doppler broadening-positron annihilation spectroscopy (DB-PAS)³⁵ in this work. DB-PAS is an established nuclear solid state technique that has been widely used to study open volumes in a variety of materials (such as, inorganic semiconductors,^{36–44} transparent conductive oxides,⁴⁵ and polymers⁴⁶) with an exceptional level of sensitivity, even enabling the detection of monovacancies. The review of Schultz *et al.* provides detailed information on the DB-PAS technique.³⁵ Highly energetic positrons generated by the beta decay of a solid ^{22}Na source are targeted at a tungsten foil to narrow their energies down to the order of a few eV. Subsequently, the positrons are accelerated by electrostatic fields to form a low-energy positron beam with kinetic energies typically on the order of 0.1–25 keV such that a thin film can be probed. Finally, the positrons are implanted into the studied material with a gradually increasing energy, resulting in increasingly larger mean implantation depths. As they thermalize (energy ~ 25 meV) in the material within ~ 1 to 3 ps, it is possible to resolve a positron implantation depth profile coming from the

film. Being the antiparticles of electrons, positrons annihilate with electrons present in the material by typically emitting two 511 keV gamma (γ) rays in opposite directions. Due to the finite kinetic energy (momentum) of the electrons with which the positrons annihilate, Doppler shifts of the 511 keV γ -ray annihilation photons are observed. Two parameters, S and W , are conventionally adopted to characterize the spectrum of the annihilation radiation. Physically, S represents the fraction of annihilation events with low-momentum electrons (small energy shift from 511 keV), which are valence electrons of atoms in the studied material, typically associated with covalent or ionic bonds.⁴⁰ Due to the expansion of the wave functions of valence electrons into any structural defects present in the probed material, the S -parameter provides sensitivity to the presence of positron trapping structural defects in the material. Furthermore, the S -parameter is sensitive to the electronic structure of the chemical phases involved. The W -parameter corresponds to annihilation events with high-momentum electrons (larger energy shift from 511 keV), which are core shell electrons of atoms in the material.⁴⁰ The W -parameter provides information on the local chemical environment of the annihilation site. The mechanism of DB-PAS is schematically illustrated in Fig. 1 which shows for simplicity, the case of positron annihilation in an atomic vacancy in a crystalline material.

With regard to hybrid organic–inorganic halide perovskites, the potential of the DB-PAS technique has been identified only recently. Dhar *et al.* utilised Positron Annihilation Lifetime Spectroscopy (PALS) and (Coincidence) Doppler Broadening ((C)DB) methods to investigate the origin of ionic conductivity⁴⁷ and the temperature-dependent electrical properties in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite.⁴⁸ A correlation was observed between open volumes present in the perovskite, identified as methylammonium vacancies (V_{MA}) and possibly involving also iodine vacancies (V_{I}), and its measured conductivity. Dhar *et al.* showed that both open volumes and conductivity of the perovskite increase with increasing temperature, and attributed the changes in its electrical response at higher temperatures to defect-mediated enhanced ionic motion.⁴⁸ Another study by Eijt *et al.* applied DB-PAS to monitor the ambient stability of CsPbBr_3 -based perovskite for 5 months in the dark, in which no significant changes in the open volumes were observed.⁴⁹ This was in accordance with the well-known fact that CsPbBr_3 perovskite is comparatively more stable than the conventional $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite in ambient conditions, primarily because of the absence of the CH_3NH_3^+ component in its lattice structure.⁵⁰

In the present work, we use DB-PAS to gain insights into the behavior of the structural degradation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films under exposure to ambient air (relative humidity of 40 to 55%) at room temperature, in particular in view of the evolution of structural defects (open volumes) and chemical changes in the perovskite films. Following up with our previous works,^{16,17} we aim to understand the role of ultrathin ALD Al_2O_3 (<1 nm) processed directly on top of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ in suppressing its environmental degradation. Furthermore, relationship of the environmental degradation with the development of open volumes in the perovskite lattice, and the

Fig. 1 Schematic showing the principle of DB-PAS illustrated for a positron annihilating in a monovacancy in a crystalline material.

changes in its chemical composition during the degradation process are discussed.

Experimental

CH₃NH₃PbI_{3-x}Cl_x perovskite sample preparation

ITO coated glass substrates are ultrasonically cleaned for 10 minutes in detergent (ExtranMA01), deionized water and iso-propanol. The compact TiO₂ layer is deposited by e-beam deposition (O₂ flow of 12 sccm, pressure of 4.7×10^{-4} mbar) at a rate of 0.05 nm s⁻¹.⁵¹ The perovskite precursor solution is made by mixing lead acetate (PbAc₂), lead chloride (PbCl₂) and methylammonium iodide (MAI) in dimethylformamide (DMF) as previously reported.⁵² The precursor solution is spincoated inside a N₂ filled glovebox on top of the TiO₂ layer at 3000 rpm for 60 s, and then annealed at 130 °C for 10 min to form the perovskite layer.

Atomic layer deposition (ALD) process of Al₂O₃

Thermal ALD Al₂O₃ is deposited on top of the perovskite at 100 °C in a FlexAL ALD reactor from Oxford Instruments. The reaction chamber is equipped with a turbomolecular pump which makes it possible to reach a base pressure of $\sim 10^{-6}$ Torr. Each ALD cycle consists of a trimethylaluminium (Al(CH₃)₃) dose of 0.04 s, followed by a purge of 15.0 s, then a H₂O vapor dose of 0.25 s, followed by a purge of 15.0 s. The thickness of the ALD Al₂O₃ layer on a c-Si substrate is characterized by *in situ* spectroscopic ellipsometry (SE) and the growth per cycle (GPC) is determined to be 0.06 nm.

Doppler broadening-positron annihilation spectroscopy (DB-PAS)

To execute the DB-PAS measurements, a variable energy positron beam (VEP) with an intensity of 10^5 e⁺ per s and a diameter of 8 mm at the position of the sample is obtained *via* moderation of

positrons, which are emitted through a tungsten foil from a ²²Na source.⁵³

Model for fitting DB-PAS data

In order to perform a quantitative analysis of the DB-PAS *S* and *W* depth profiles, the software package VEPFIT is used.⁵⁴ The depth profiles are fitted using model 5 of the VEPFIT package which assumes that the samples have a layered structure and each layer has a constant *S*- and *W*-parameter. In order to fit the PAS data, the following assumptions are made. First, it is assumed that during the decomposition process the thickness of the perovskite layer does not remain constant, since volatile reaction products can effuse from the layer. Cross-sectional SEM measurements performed on the layer stacks comprising of glass/ITO/TiO₂/perovskite and glass/ITO/TiO₂/perovskite/ALD Al₂O₃ showed that during the degradation process, the perovskite layer experiences a clear reduction in its thickness (from ~ 270 nm to ~ 210 nm after 22 days of air exposure), validating our above assumption. The corresponding SEM images can be found in Fig. S1 (ESI†). Therefore, during the fitting procedure both the *S*- and *W*-parameters of the perovskite layer, and the thickness of the perovskite layer as a function of the air exposure time are considered to be “free” parameters. The fit model assumes that the perovskite can be fitted as a single layer. Meanwhile, little is known about the positron diffusion length in the perovskite layer. Based on our SEM analysis, which show that the initial layer thickness of the perovskite layer on day 0 is approximately 270 nm, we have used this thickness as a fixed parameter in the fit to determine the positron diffusion length in the perovskite layer. The value of the positron diffusion length which fits the data in the most accurate way is 50 nm. This value is subsequently kept constant during the fitting process of the depth-profiles at various stages of the degradation process. A perovskite density of 4.0 g cm⁻³ is

used for the analysis. During the fit process, the TiO_2 and ITO layers are treated as one effective layer due to the fact that the TiO_2 layer is much thinner than the ITO layer (50 nm and 150 nm, respectively). In addition, these layers are present underneath the ~ 270 nm perovskite in the investigated layer stack, making it hard to resolve the two distinct layers in the positron experiments. The thickness of the TiO_2 /ITO effective layer is assumed to remain constant during the degradation process at a value of 200 nm, as is confirmed by the SEM analysis. Previous positron depth profile measurements on bare TiO_2 and ITO showed that the positron diffusion length for such materials is in the range of few nm.^{55,56} Thus, for the present study, the diffusion length in the TiO_2 /ITO layer is fixed at 5 nm. A weighted average density value of 6.41 g cm^{-3} is used for the combined TiO_2 /ITO layers taking into account the density and the thickness of each layer. During the fit process, the S - and W -parameters of the effective TiO_2 /ITO layer that were determined to be equal to 0.511 and 0.061, respectively, are used. These values are acquired from the DB-PAS depth-profiles measured on a sample containing only the TiO_2 /ITO layer deposited on glass substrate (Fig. S2, ESI†). For the glass substrate the S -parameter and W -parameter are also kept fixed at a value of 0.530 and 0.0549, respectively, during the VEPFIT analysis. A density of 2.4 g cm^{-3} and a positron diffusion length of 20 nm are used for the glass substrate. All the DB-PAS data are fitted by using a three-layer fit model. This model consisting of the perovskite layer, the TiO_2 /ITO effective layer, and the glass substrate with an infinite depth range, is a simple representation of the sample configuration which is investigated in this work. The surface annihilation parameters S_{surf} and W_{surf} are assumed to include the characteristics of positron annihilation associated with the ultrathin (< 1 nm) ALD Al_2O_3 top layer.

X-ray diffraction (XRD)

XRD analysis is carried out using a PANalytical X'Pert Pro MRD X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$) in the 2θ range 10° to 60° at a scanning rate of $1.5^\circ \text{ min}^{-1}$.

X-ray photoelectron spectroscopy (XPS)

XPS measurements are carried out in a Thermo Scientific K-Alpha system, equipped with an Al X-ray source ($\text{K}\alpha$, 1486.6 eV) with a photoelectron take-off angle (θ) of 90° , without any pre-sputtering. Such experimental conditions enable an investigation of the perovskite depth within ~ 10 nm below its surface.^{19,57} Binding energy is corrected with respect to adventitious carbon (C1s) at 284.8 eV.

Results and discussion

First, the bulk and surface stability of the perovskite films are investigated with and without ALD Al_2O_3 . The layer stack employed in this work consists of glass/150 nm Sn doped indium oxide (ITO)/ ~ 50 nm compact TiO_2 / ~ 300 nm $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite/18 cycles of ALD Al_2O_3 (thickness < 1 nm). Fig. 2a presents the XRD spectra of the pristine perovskite and perovskite/ALD

Fig. 2 XRD spectra of the pristine perovskite and perovskite/ Al_2O_3 film (a) at day 0 and (b) after 22 days of exposure to ambient air (relative humidity of 40–55%) at room temperature.

Al_2O_3 films at day 0. No change in crystallinity of the bulk perovskite is recorded after ALD processing, which is in good agreement with our previous studies.^{16,17} Fig. 2b presents the XRD spectra of the perovskite and perovskite/ALD Al_2O_3 films after 22 days of exposure to ambient air (relative humidity in the range of 40–55%) at room temperature. The degradation of the perovskite film is clearly evident from the appearance of a high intensity signature peak at 12.6° , assigned to the (001) diffraction peak of PbI_2 , which results from the decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ when exposed to oxygen and moisture. In parallel, the intensity of the characteristic peak at 14.1° , which corresponds to the (110) plane of tetragonal $\text{CH}_3\text{NH}_3\text{PbI}_3$, experiences a significant decrease. On the contrary, in the perovskite film decorated with ALD Al_2O_3 , the 14.1° $\text{CH}_3\text{NH}_3\text{PbI}_3$ (110) peak is clearly demonstrated to have a higher intensity than the 12.6° PbI_2 peak, indicating that the presence of Al_2O_3 suppresses the bulk degradation of the perovskite under exposure to ambient air.

In order to gain insight into the changes in perovskite chemical composition, XPS analysis is carried out on both the

investigated samples at day 0 and after 22 days of exposure to ambient air, with a photoelectron take-off angle (θ) of 90° , enabling a sampling depth down to ~ 10 nm.^{19,57} The presence

of ALD Al_2O_3 is confirmed by the characteristic $\text{Al}2\text{p}$ peak at 74.6 eV as shown in Fig. S3 (ESI[†]). Fig. 3a presents the $\text{N}1\text{s}$ core level spectra for the pristine perovskite before and after 22 days

Fig. 3 Surface XPS spectra of (a), (b) $\text{N}1\text{s}$, (c), (d) $\text{C}1\text{s}$ and (e), (f) $\text{I}3\text{d}$ peaks of the pristine perovskite and perovskite/ $\text{ALD Al}_2\text{O}_3$ films at day 0 and after 22 days of exposure to ambient air (relative humidity of 40–55%) at room temperature. Open circles, solid lines and dashed lines are measured data, peak fits and cumulative fits, respectively.

of ambient air exposure (relative humidity of 40–55%) at room temperature. The peak at binding energy (B.E.) of 402.7 eV, representative of the N–C bonds in the perovskite, disappears upon air exposure. A similar behavior is observed in the C1s spectra shown in Fig. 3c, where the disappearance of the characteristic C–N B.E. peak at 286.6 eV is evident. These two observations confirm the decomposition of the perovskite, led by the effusion of CH_3NH_2 . Meanwhile, comparatively higher surface stability of the perovskite/ALD Al_2O_3 film is witnessed, marked by the persistence of the characteristic N–C and C–N B.E. peaks even after 22 days of exposure to ambient air (Fig. 3b and d), indicating reduced CH_3NH_2 effusion from the perovskite surface. In parallel, the appearance of a new peak at B.E. of 399.5 eV in the N1s spectra of the perovskite/ALD Al_2O_3 film (Fig. 3b) is attributed to the formation of primary or secondary amines as a result of the perovskite degradation process.⁵⁸ At the same time, the increase in the area of the C–C B.E. peak at 284.8 eV and the formation of the O–C=O B.E. peak at 288.4 eV in both the investigated samples (Fig. 3c and d) is ascribed to the contamination of adventitious carbon when exposed to ambient air. When comparing the I3d spectra of the two investigated films after 22 days of air exposure (Fig. 3e and f), the decrease of the peak areas is evident only in case of the pristine perovskite. This indicates that in the absence of ALD Al_2O_3 , effusion of iodine (in the form of HI or I_2) occurs from the perovskite surface.

Having confirmed the effect of Al_2O_3 on the bulk and surface stability of the perovskite, the modification of the perovskite morphological structure is further investigated by employing the DB-PAS technique. The *S*-parameter and *W*-parameter collected as a function of positron implantation energy (E_{positron}) are analyzed using the VEPFIT program,⁵⁴ assuming a three layered structure consisting of the perovskite layer, the TiO_2/ITO layer, and the glass substrate. Since the ALD Al_2O_3 is ultrathin (<1 nm), it cannot be accurately resolved as an individual layer in DB-PAS. Therefore, it is reasonable to include the positron annihilation associated with the ALD Al_2O_3 as a contribution to the surface annihilation represented by S_{surf} and W_{surf} in the model. Fig. 4 presents the Doppler broadening depth-profiles, $S(E)$ and $W(E)$, of the pristine and Al_2O_3 decorated perovskite. The fitted curves are in good agreement with the acquired depth-profiles, indicating that the model used in the VEPFIT program is an acceptable approximation of the layer stack studied in this work. Three regions can be identified in Fig. 4: the surface annihilation characterized by the surface parameter (S_{surf}) which dominates the lowest positron energies <0.5 keV (blue region), the *S* value in the range of 0.5–5 keV which represents annihilation of positrons in the perovskite film (yellow region), and the decrease in the *S*-parameter beyond 5 keV due to increasingly larger fractions of the positrons annihilating in the TiO_2/ITO underlayers and the glass substrate (grey region). When comparing the depth-profiles of the pristine perovskite and perovskite/ALD Al_2O_3 (day 0), it can be concluded that the differences are negligible compared to the typical shifts in the *S*- and *W*-parameters obtained upon development of cation

Fig. 4 DB-PAS depth-profiles of *S*- and *W*-parameters of the pristine perovskite and perovskite/ALD Al_2O_3 film at day 0. Full lines are fit curves obtained by VEPFIT analysis. The blue region is dominated by positron annihilation at the surface, the yellow region by positron annihilation in the perovskite film, and the grey region by increasingly larger fractions of the positrons annihilating in the TiO_2/ITO underlayers and the glass substrate.

vacancies (for example, Zn monovacancies,^{59,60} divacancies and multivacancies in hydrogenated $\text{Si}^{37,61}$). Hence, these very minor shifts in the $S(E)$ and $W(E)$ plots (Fig. 4) confirm that the processing of ALD Al_2O_3 (<1 nm) directly on top of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite does not lead to any significant changes in the perovskite layer. The results are in agreement with our recent work, where we showed *via* infrared spectroscopy and XRD studies that the bulk degradation of the perovskite during the growth of ALD Al_2O_3 is negligible under the very low relative humidity conditions (maximum of 0.1%) which we adopted in the ALD recipe.⁶²

Subsequently, both the samples are investigated by monitoring the evolution of the Doppler depth profiles over a period of 22 days under exposure to ambient air (40–55% relative humidity) at room temperature. In Fig. 5a, the $S(E)$ and $W(E)$ plots experience a shift towards lower E_{positron} as a function of air exposure time. This indicates a decrease in the thickness of the perovskite layer, as it is evident from the increasingly lower implantation energies required for the positrons to reach and annihilate in the underlying TiO_2/ITO substrate. This points to a loss of mass in the perovskite layer that arises from the effusion of volatile decomposition products (CH_3NH_2 , HI, I_2) and the formation of PbI_2 upon exposure to humid air. When the DB-PAS depth profiles of the

Fig. 5 DB-PAS depth-profiles of S - and W -parameters of (a) pristine perovskite and (b) perovskite/ALD Al_2O_3 film at day 0 and after 3, 6, 12 and 22 days of air exposure (relative humidity of 40–55%) at room temperature. The time evolution is indicated by the direction of the arrow. Full lines are fit curves obtained by VEPFIT. The blue region is dominated by positron annihilation at the surface, the yellow region by positron annihilation in the perovskite film, and the grey region by increasingly larger fractions of the positrons annihilating in the TiO_2 /ITO underlayers and the glass substrate.

pristine perovskite (Fig. 5a) and perovskite/ALD Al_2O_3 (Fig. 5b) are compared, it can be observed that the shifts in the $S(E)$ and $W(E)$ plots occur only after a longer air exposure time in case of the Al_2O_3 capped sample, indicating that the presence of Al_2O_3 delays the decrease in perovskite film thickness under exposure to ambient air. As obtained from VEPFIT modelling, the thickness of the pristine perovskite at day 0 is 271 ± 1 nm, at day 12 is 235 ± 1 nm and at day 22 is 212 ± 1 nm. For the perovskite films capped with ALD Al_2O_3 , the thickness of the perovskite at day 0 is 277 ± 1 nm, at day 12 is 266 ± 1 nm and at day 22 is 216 ± 1 nm, which points out a delay in the thickness reduction over time. The thickness of the perovskite derived from VEPFIT modelling is in agreement with the thickness determined from the cross-sectional SEM images performed on both pristine perovskite and perovskite/ Al_2O_3 stacks as shown in Fig. S1 (ESI[†]), demonstrating a thickness decrease from ~ 270 nm at day 0 to ~ 210 nm at day 22.

In addition to the shifts in the $S(E)$ and $W(E)$ plots in Fig. 5(a and b) indicating a decrease in the thickness of the perovskite layer, subtle changes in the S and W -parameters are also evident in the range of 0.5–5 keV (representing annihilation of positrons in the perovskite film). A decrease in the S -parameter is observed which is complemented by an increase in the W -parameter, indicating changes in open volumes and

chemical composition in the perovskite. In order to quantify these subtle changes in the S - and W -parameters, VEPFIT modelling is used. The changes in the fitted S -parameter ($\Delta S/S_0$) over time defined as $(S_{\text{day } x} - S_{\text{day } 0})/S_{\text{day } 0}$, and the changes in the fitted W -parameter ($\Delta W/W_0$) over time defined as $(W_{\text{day } x} - W_{\text{day } 0})/W_{\text{day } 0}$ are investigated for both pristine and perovskite/ Al_2O_3 samples. Fig. 6a shows that $\Delta S/S_0$ is negative and the magnitude increases as a function of air exposure time. It is known from previous studies that positron annihilation is very sensitive to the detection of methylammonium vacancies in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite.^{47,48} At the same time, theoretical and experimental reports have shown that also other types of ionic vacancies, including lead and iodine vacancies could initiate the environmental degradation process in the hybrid perovskite films.^{31–33} The negative $\Delta S/S_0$ suggests a decrease in the open volumes in the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ lattice when exposed to air, which could be caused by the ingress of H_2O molecules into its cation vacancies (such as, methylammonium vacancies). Furthermore, chemical transformation of the perovskite film upon exposure to humid air, involving the formation of a relatively dense PbI_2 phase and possibly also the formation of a perovskite hydrate ($\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$) phase at relative humidity of 40%,⁶³ are expected to contribute to the observed decrease in S -parameter.

Fig. 6 (a) $-\Delta S/S_0$, (b) $\Delta W/W_0$ and (c) S - W plots of the pristine perovskite and perovskite/ALD Al₂O₃ film as a function of number of days of ambient air exposure (relative humidity of 40–55%) at room temperature. (d) $-\Delta S/S_0$ and $\Delta W/W_0$ of the perovskite/ALD Al₂O₃ film on day 22 as a function of number of Al₂O₃ cycles deposited on top of the perovskite. S_0 and W_0 are the Doppler parameters of the as-deposited perovskite film. Dashed lines are guides to the eye.

Monitoring the changes in W -parameter in Fig. 6b, it is seen that $\Delta W/W_0$ is positive and the magnitude increases as a function of air exposure time. This could be attributed to chemical changes in the perovskite involving the formation of a relatively dense PbI₂ layer upon exposure to ambient air. Indeed, the XRD data of Fig. 1b clearly show the formation of PbI₂ upon air exposure, and the increased contribution of positron annihilation with Pb5d electrons will lead to an increase in the W -parameter, and the more dense nature of PbI₂ compared to CH₃NH₃PbI₃ may induce a complementary decrease in the S -parameter. When both the investigated layer stacks are compared, it is clear that the changes in the open volumes and chemical composition are significantly reduced in the perovskite film decorated with ALD Al₂O₃, which is ascribed to less filling of the open volumes (primarily the cation vacancies) by the infiltrating H₂O molecules, complemented with a smaller change in chemical composition because of reduced decomposition of the perovskite.

S - W plots are commonly utilized in PAS research community to provide a more convenient overview about phase transformations

and/or variation in the size or concentration of vacancy-related open volumes in the material. To present the effectiveness of the Al₂O₃ capping layer as a means to mitigate the degradation of the perovskite, S - W maps of both the investigated samples are shown in Fig. 6c. It is evident that after 22 days of air exposure, the final S - W point of the perovskite/Al₂O₃ sample deviates much less from its initial S - W point, when compared to the pristine perovskite sample. This again confirms that the changes in chemical composition and open volumes in the perovskite are significantly less when it is capped with ALD Al₂O₃. Finally, the number of ALD cycles is varied to assess the effect of the Al₂O₃ thickness on the perovskite stability. As seen in Fig. 6d, after 22 days of exposure to ambient air, the perovskite sample capped with the thickest Al₂O₃ layer experiences the smallest changes in $-\Delta S/S_0$ and $\Delta W/W_0$, and hence, an enhanced environmental stability (in the studied range of ALD cycles), suggesting that thicker ALD Al₂O₃ is more effective in suppressing the occupation of H₂O molecules into the open volumes of the perovskite and the subsequent chemical transformations in the layer.

Conclusions

DB-PAS is utilized to investigate the structural degradation of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films, associated with the development of structural defects (or open volumes) and chemical transformations under exposure to ambient air (relative humidity 40–55%) for a period of 22 days at room temperature. The DB-PAS depth profiles, *i.e.*, $S(E)$ and $W(E)$ plots shift towards lower implantation energies as a function of air exposure time, indicating a decrease in the thickness of the perovskite layer. This is corroborated by XPS analysis of the perovskite films showing the effusion of volatile decomposition products (CH_3NH_2 , HI, I_2) under exposure to ambient air. In addition, a decrease in the S -parameter is observed over time, suggesting the ingress of H_2O molecules into the open volumes present in the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ lattice. The S -parameter is furthermore affected by the chemical transformations of the perovskite layer. This is complemented by an increase in the W -parameter indicating changes in the chemical composition of the films due to the formation of a relatively dense PbI_2 layer (corroborated by XRD). Meanwhile, the changes in the S - and W -parameters are significantly smaller when the perovskite film is capped with ALD Al_2O_3 (< 1 nm). The DB-PAS results demonstrate that the presence of ALD Al_2O_3 on top of the perovskite suppresses the ingress of H_2O molecules into the open volumes, while delaying the reduction of the perovskite film thickness resulting from its chemical transformations when exposed to the ambient environment. Our study indicates that the use of DB-PAS in connection with other conventional characterization techniques, such as XRD and XPS, may substantially help in gaining further understanding of the degradation mechanism of different state-of-the-art perovskite chemical compositions.

Conflicts of interest

There are no conflicts to declare.

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