The chemistry and energetics of the interface between metal halide perovskite and atomic layer deposited metal oxides

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The chemistry and energetics of the interface between metal halide perovskite and atomic layer deposited metal oxides ^F

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ABSTRACT

The chemistry of the interface between the metal halide perovskite absorber and the charge transport layer affects the performance and stability of metal halide perovskite solar cells (PSCs). The literature provides several examples of poor PSC conversion efficiency values, when electron transport layers (ETLs), such as SnO₂ and TiO₂, are processed by atomic layer deposition (ALD) directly on the perovskite absorber. In the present work, we shed light on the chemical modifications occurring at the perovskite surface, during ALD processing of SnO₂ and TiO₂, in parallel with the evaluation of the PSC cell performance. The ALD processes are carried out on a (Cs₃FA)Pb(I,Br)₃ perovskite by adopting tetrakis(dimethylamino)tin(IV) and tetrakis(dimethylamino)titanium(IV) as metal precursors and H₂O as the coreactant for SnO₂ and TiO₂, respectively. Perovskite surface modification occurs in the form of an ultrathin PbBr₂ layer. Furthermore, in the case of SnO₂, halogen molecules are detected at the interface, in parallel with the initial growth of an oxygen-deficient SnO₂. Subgap defect states just above the valence band maximum of SnO₂ are also detected. These states act as hole traps at the perovskite/SnO₂ interface, subsequently promoting charge recombination and deteriorating the performance of the cell. We hypothesize that a redox reaction between the perovskite, or its decomposition products, and the Sn metal center of the ALD precursor takes place: I[−] and Br[−] are oxidized to I₂ and Br₂, respectively, and Sn(IV) is reduced to Sn(II). In contrast, the Ti(IV) metal center does not undergo any redox process, and, as a result, a promising 11% power conversion efficiency is measured with TiO₂ as the ETL. This result strongly suggests that TiO₂ may be a more suitable ETL, when processed directly on the perovskite absorber.

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I. INTRODUCTION

Over a relatively short period of about ten years, metal halide perovskite solar cells (PSCs) have been successful in gaining widespread attention in the photovoltaic (PV) community, with a current record efficiency of over 25%.¹ This accomplishment has been the result of both fundamental understanding of the metal halide perovskite material itself (in terms of crystal growth, chemical composition, and optoelectronic properties)² and improved engineering of the device architecture. The latter includes novel

interfacial design approaches and the development of efficient charge transport and electrode layers.^{2–4} In this specific case, the use of thin films processed by atomic layer deposition (ALD) has been particularly alluring, a manifestation of which is the extensive application of ALD in PSCs, which is showcased by a number of publications on this topic over the last years,^{5–14} starting from 2014.¹⁵

Inherently conformal and pinhole-free films processed by ALD have been applied either as electron transport layers (ETLs) in an “n-i-p” solar cell configuration or as hole transport layers (HTLs) in a “p-i-n” solar cell configuration,^{9,11} where “n”

corresponds to the ETL, “i” to the intrinsic perovskite absorber, and “p” to the HTL. In addition, these films, when applied on top of perovskites in combination with an organic charge transport interlayer (CTL) (such as [6,6]-phenyl-C₆₁-butyric acid methyl ester, PCBM, or C₆₀) in a p-i-n configuration, have been shown to provide several improvements.⁷ These are good charge extraction, reduced potential damage to the sensitive underlying layers during sputtering of the transparent top electrode, and excellent barrier properties against moisture and thermal stress. This has enabled the engineering of highly efficient and environmentally stable perovskite-based single-junction and tandem devices.^{6,7,14–20}

At the same time, the presence of organic ETLs in p-i-n cells may in some cases introduce parasitic absorption losses and potential shunting pathways, especially when large area devices are fabricated.²¹ In addition, PSCs that contain organic ETLs have generally exhibited very poor mechanical properties.²² Therefore, recently, there has been widespread interest in the application of inorganic ETLs processed by ALD directly on top of the perovskite absorber, i.e., without the addition of organic interlayers. However, to date, the achieved power conversion efficiencies (PCEs) in this device configuration fall between 0.5% and 8.2% (Table I).^{8,10} The underlying reasons are not very clear yet. A contributing factor is expected to be the chemical modification that occurs at the surface (or even bulk) of the perovskite during ALD processing directly on top of the perovskite.

Progress has already been made in this field. For example, several studies have focused on the chemical modifications occurring in the perovskite upon direct growth of Al₂O₃ on top of the perovskite. So far, Al₂O₃ is considered the only successful case of direct ALD processing on the perovskite absorber.^{12,23–25} A recent work from our group using infrared (IR) and x-ray photoelectron spectroscopy (XPS) analysis revealed that the interaction between H₂O (used as coreactant) and CH₃NH₃PbI_{3–x}Cl_x was negligible under the conditions adopted in the ALD recipe.²⁶ On the contrary, exposure to trimethylaluminum (TMA, used as metal precursor) was found to degrade the perovskite surface, leading to the effusion of methylammonium (MA) cations.^{26,27} In parallel, it was shown that TMA and H₂O do not diffuse into the bulk of the perovskite.^{26–28} Furthermore, by means of *in situ* quartz crystal microbalance (QCM) and IR spectroscopy, it was shown that the TMA molecules etch the CH₃NH₃PbI_{3–x}Cl_x perovskite surface at 75 °C.²⁷ A similar behavior was reported by Yu *et al.*²⁹ Synchrotron

XPS analysis was employed by Kot *et al.*,³⁰ which indicated that the interaction of ALD precursors occurs only at the surface of the CH₃NH₃PbI₃ and FA_{0.85}MA_{0.15}Pb(Br_{0.15}I_{0.85})₃ perovskite (where FA corresponds to the formamidinium cation) during the growth of Al₂O₃ at room temperature.^{23,24} In parallel, they showed that there is covalent bonding at the CH₃NH₃PbI₃/Al₂O₃ interface. At the same time, they identified a charge balance between the polaronic and excitonic states in CH₃NH₃PbI₃ and Al₂O₃.²³

In the case of ETLs, the chemistry of the metalorganic precursor plays a critical role.^{5,8,10} For ZnO, the diethyl-Zn (DEZ) precursor strongly reacted with the organic component of the hybrid perovskite leading to its complete decomposition. This was witnessed for both CH₃NH₃PbI₃ and (MA,FA)Pb(I,Br)₃-based perovskite systems.^{8,10} Moreover, even after 100 cycles, no growth of ZnO was detected on the CH₃NH₃PbI₃ perovskite.⁸ Yu *et al.*³¹ investigated the nucleation of ZnO on top of the CH₃NH₃PbI₃/PCBM layer. By performing IR and QCM analyses, they showed that ZnO did not readily grow even on top of PCBM. However, the PCBM blocked the DEZ precursor from abstracting the organic cation of the perovskite. In contrast to DEZ, they observed that TMA could readily react with the carbonyl group of PCBM. Therefore, they employed Al₂O₃ as a seeding layer on top of PCBM coated CH₃NH₃PbI₃ in order to achieve the nucleation of ZnO.

Another metal oxide that has been adopted as a potential ETL is TiO₂, although always in combination with a PCBM or C₆₀ interlayer.^{7,20,32–35} The ALD process involved the application of tetrakis(dimethylamino)titanium(IV) (TDMA-Ti) and H₂O, as the metalorganic precursor and coreactant, respectively. Despite these promising results in combination with organic interlayers, to the best of our knowledge, TiO₂ grown directly on top of the absorber has not been used as sole ETL. Thus, the perovskite/TiO₂ interface has been so far a limited subject of investigation.^{33,35,36}

Among all ETLs grown directly on perovskites, SnO₂ is the most investigated. Palmstrom *et al.*¹⁰ adopted tetrakis(dimethylamino)tin(IV) (TDMA-Sn) as the metal precursor for SnO₂ and identified that effusion of the FA cation from the Cs_{0.17}FA_{0.83}Pb(Br_{0.17}I_{0.83})₃ perovskite occurs at temperatures of 100 °C and above during the ALD process. With regard to the thermal stability of the perovskite, the authors reported the formation of crystalline PbI₂ upon vacuum annealing of the perovskite at 150 °C, which is in

TABLE I. PV parameters of p-i-n PSCs with SnO₂ and TiO₂ serving as ETLs directly grown on the perovskite: data from the literature and values from this work. PV parameters are reported for reverse scan only. All metal oxide films were grown using H₂O as the coreactant. TDMA-Sn and TDMA-Ti precursors were used for SnO₂ and TiO₂, respectively. The first column refers to the perovskite composition: (1) FA_{0.83}MA_{0.17}Pb(I_{0.83}Br_{0.17})₃; (2) Cs_{0.17}FA_{0.83}Pb(I_{0.5}Br_{0.5})₃; (3) Cs_{0.17}FA_{0.83}Pb(I_{0.83}Br_{0.17})₃; (4) and (5) Cs_{0.15}FA_{0.85}Pb(I_{0.92}Br_{0.08})₃.

	Growth T (°C)	PSC architecture	V _{OC} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)	Reference
1	120	NiO _x /perovskite/SnO ₂ /Au	0.48	19.0	43	4.0	8
2	100	NiO _x /perovskite/SnO ₂ /ZTO/Au	0.97	15.9	53.4	8.2	10
3	80	NiO _x /perovskite/SnO ₂ /ITO/Ag	0.73	2.9	24.5	0.5	10
4	100	PTAA/perovskite/SnO ₂ /Al	0.90	15.1	43	5.9	This work
5	100	PTAA/perovskite/TiO ₂ /Al	0.92	19.8	75	13.6	This work

line with the findings from Kot *et al.*³⁷ On the contrary, Hultqvist *et al.*⁸ reported no detrimental effect on the bulk or surface stability [by employing x-ray diffraction (XRD) and XPS, respectively] of an (MA,FA)Pb(I,Br)₃ perovskite when exposed to TDMA-Sn within a temperature window of 85–150 °C. From XPS depth profile analysis, they suggested the possibility of halogen incorporation into the SnO₂ film in the early growth stage.

Both works, despite reporting contrasting results in terms of chemical modifications during ALD, showed that limited solar cell performances were achieved upon direct ALD processing on perovskites. Hultqvist *et al.* reported a PCE of 3.4%, which was raised to 7.8% after performing biasing treatments on the cells (Table I).⁸ Palmstrom *et al.* investigated different SnO₂ deposition parameters and two perovskite compositions in their devices, leading to a limited cell efficiency of 8.2% (Table I).¹⁰ Both studies cited energy barriers as potential issues in their cells: band diagrams, constructed partially from literature data, showed a potential conduction band maximum (CBM) misalignment at the perovskite/SnO₂ interface.^{8,10} However, it should be noted that a favorable energy level alignment is not the only condition to be fulfilled. Often, interface defects,³⁸ responsible for nonradiative charge recombination, can severely affect the cell performance. In this respect, the role of PCBM is to serve as an ETL and a passivation layer for trap states at the interface between the perovskite and the metal oxide.³⁹ All the above-mentioned studies related to the processing of SnO₂ directly on top of the perovskite have laid the groundwork for understanding the perovskite/ETL systems. Moreover, they strongly suggest that the factors contributing to poor PSC performance are not yet fully understood and need further investigation. With the present contribution, we aim to systematically elucidate the chemical changes occurring in the bulk and surface of hybrid perovskite substrates upon ALD processing of ETLs, such as SnO₂ and TiO₂ using metalorganic precursors with the same ligand chemistry, TDMA-Sn and TDMA-Ti, and H₂O as the coreactant. Concurrently, we aim to identify the effect of these changes on the energetics of the perovskite/metal oxide systems and on the cell performance. We select a Cs_{0.15}FA_{0.85}Pb(I_{0.92}Br_{0.08})₃ perovskite, because of its wide application in several literature studies, which also involved SnO₂ and TiO₂ as ETLs. We begin our work by comparing the cell performance with the employed metal oxide ETLs. Next, we identify the chemical changes that the perovskite absorber undergoes upon ALD processing by means of XPS. The latter is also adopted to determine the chemical composition of extremely thin SnO₂ and TiO₂ films. Finally, the energetics of the perovskite/metal oxide systems are estimated using ultraviolet photoelectron spectroscopy (UPS).

We found that the growth of SnO₂ and TiO₂ does not affect the bulk of the metal halide perovskite and only a thin interfacial PbBr₂ layer is formed. Despite the similar chemistry of the selected ALD precursors, we show that in the case of perovskite/SnO₂, we detect the formation of Br₂ and I₂, in the proximity of the perovskite/SnO₂ interface. Along with that, the initial growth of SnO₂ on the perovskite is characterized by the formation of an oxygen-deficient film accompanied by the presence of subgap states near the valence band maximum (VBM) of SnO₂, which are assigned to reduced Sn(II) states. We relate the presence of such defect states to a redox reaction taking place between the halide species Br[−] and I[−]

of either the perovskite or its decomposition products and the Sn(IV) metal center of the ALD precursor. The accumulation of molecular halides at the perovskite/SnO₂ interface and the growth of SnO₂ that exhibits subgap defects are responsible for the compromised cell performance and s-shaped J-V curves when SnO₂ is used as the sole ETL. Instead, when TiO₂ is grown directly on the perovskite, the above-mentioned redox process does not occur. As a matter of fact, cells employing TiO₂ deliver efficiencies overcoming the highest values reported so far for metal oxide CTLs processed directly on top of the perovskite, with an 11% PCE deduced from maximum power point tracking (MPPT).

II. EXPERIMENT

A. Perovskite solar cell fabrication

The device fabrication begins with ultrasonically cleaning the patterned glass/ITO substrates (Naranjo Substrates, 13–15 Ω/sq) with soap water, de-ionized water, and isopropanol, which is followed by a UV-ozone treatment for 30 min. The manipulations that follow are performed inside a nitrogen-filled glovebox. A poly(triarylamine) (PTAA) solution in toluene 2 mg/ml (Sigma-Aldrich) is spin coated on the glass/ITO substrates at 5000 rpm for 30 s and annealed at 100 °C for 10 min. Afterward, the dual cation perovskite Cs_{0.15}FA_{0.85}Pb(I_{0.92}Br_{0.08})₃ solution is prepared by mixing a 1.33M concentration of the following precursors: PbBr₂ (99.9%) and PbI₂ (99.999%), both from TCI; FAI (99.9%) and FABr (99.9%) both from Greatcell (Dyesol); and CsI (99%, Sigma-Aldrich), in anhydrous DMF:DMSO (vol. ratio = 9:1), followed by stirring overnight at room temperature. The perovskite solution is then spin coated with a two-step procedure: at 2000 rpm for 10 s and at 5000 rpm for another 30 s. During the second step, 300 μl of chlorobenzene is poured on the spinning substrate 20 s prior to the end of the program. The film is then annealed on a hot plate at 100 °C for 10 min. For the devices employing a PCBM interlayer, a 20 mg ml^{−1} PCBM (Solenne B.V., 99%) solution in chlorobenzene is spin coated onto the perovskite layer at 1500 rpm for 50 s. Next, metal oxide layers are grown either directly on the perovskite or on an overlying PCBM film. For the reference device, a bathocuproine (BCP) solution in ethanol (0.5 mg/ml) was spin coated at 3000 rpm for 40 s. Afterward, 100 nm of Cu (after BCP spin-coating) or 100 nm of Al (after ALD of metal oxide layers) electrode is thermally evaporated at a pressure of 10^{−6} mbar. In both cases, a shadow mask was used for electrode deposition.

B. Metal oxide deposition

TDMA-Sn (99.9%, STREM Chemicals) is used as the metalorganic precursor for the SnO₂ thin film deposition and TDMA-Ti (99.9%, STREM Chemicals) is used for TiO₂. The interface analysis studies are also carried out for Al₂O₃ grown with dimethylaluminum isopropoxide (98%, Dockweiler Chemicals) as a precursor, which delivers good performances in n-i-p cells, as we have reported previously.⁴⁰ H₂O is used as the coreactant for all the ALD processes. The processes are carried out taking into account the thermal sensitivity of the perovskite absorber setting the reactor chambers and substrate tables to 100 °C.¹⁰ The ALD reactor

used for SnO_2 and Al_2O_3 growth is OpAL, and for TiO_2 , Flexal2 is used (both from Oxford Instruments). The details of the ALD processes are described in detail in Sec. I in the supplementary material.⁷³

C. Characterization techniques

The structure of the pristine perovskite and the perovskite/metal oxide layers is evaluated by XRD using a PANalytical X'Pert Pro MRD system, with $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) in the 2θ range of 10° – 60° , with a step size of 0.02° .

The surface composition of the metal oxides grown on crystalline silicon (c-Si) and on perovskite is investigated by means of XPS in a Thermo Scientific K-Alpha system, equipped with an Al $\text{K}\alpha$ x-ray source (1487 eV) without any presputtering for a series of samples with different metal oxide thicknesses. Using THERMO AVANTAGE software, each spectral feature is fitted with Gaussian/Lorentzian mixed peaks, which have a fixed full width half maximum for each chemical state across all the pristine perovskite and perovskite/metal oxide samples. For each perovskite/metal oxide sample, unless specified otherwise, the binding energies (BE) of spectral features are aligned such that the perovskite $\text{I-3d}_{5/2}$ spectral feature occurs at 619.5 eV (as it does in the pristine perovskite) rather than aligning to adventitious carbon for the sake of comparison of the spectra.⁴¹ Details regarding peak alignment are shown in Sec. II in the supplementary material.⁷³ The thickness of the films grown on top of the perovskite is determined in the same manner as in a previous publication.²⁶

UPS measurements are performed in a VG EscaLab II system (Thermo Fisher Scientific Inc.) with a base pressure of 10^{-8} Pa, using He-I radiation (21.22 eV) and -6 V bias. The collected information regarding the work function and ionization energy are used to obtain the Fermi level (E_F) and valence band maximum positions for the pristine perovskite and perovskite/metal oxide systems.

The electrical characterization of the completed solar cells is performed under a solar simulator calibrated to AM 1.5 using a commercial c-Si reference cell (ReRa Solutions, IEC 60904-9 compliant and certified) and using a Keithley 2400 source meter to collect the current-voltage (J-V) curves. The J-V curves are measured in both scan directions: (i) reverse scan from 1.2 to -0.2 V and (ii) forward scan from -0.2 to 1.2 V , and the scan rate is kept at 200 mV/s . Prior to the J-V scans, the PCE deduced from the maximum power point measurement was tracked for 120 s. All the PV measurements are performed while masking the active area with an aperture of 0.09 cm^2 in a metal mask and at room temperature.

III. RESULTS

A. Performance of perovskite cells with ETLs

The SnO_2 and TiO_2 layers are first tested as ETLs in combination with a PCBM interlayer in a p-i-n cell architecture, in order to compare our results with the relevant literature and with the reference cell without a metal oxide layer. All cell architectures are reported in Fig. S2, Sec. III, in the supplementary material.⁷³ 20 nm-thick metal oxide layers in combination with PCBM are incorporated into the perovskite cells. The corresponding J-V curves are shown in Fig. 1: only a small hysteresis is observed in all

FIG. 1. J-V curves of p-i-n perovskite solar cells with the configurations shown in Figs. S2(a)–S2(b), Sec. III, in the supplementary material (Ref. 73). The metal oxide thickness is 20 nm.

cases. The use of metal oxides results in similar PCEs: 16.1% (reverse scan) and 16.0% (deduced from MPPT, note that all MPPT are shown in Fig. S3, Sec. IV, in the supplementary material⁷³) for SnO_2 ; 15.6% (reverse scan) and 15.5% (MPPT) for TiO_2 versus 16.5% (reverse scan) and 16.1% (MPPT) for the reference cell. The performance of the cells with both metal oxides is consistent with the results in the literature and comparable to the performance of the cell with the organic ETL only.^{17,19,20} All three J-V curves exhibit negligible hysteresis. The adoption of TiO_2 results in lower fill factor (FF) possibly related to the lower conductivity of amorphous TiO_2 , when compared to SnO_2 . Thus, we confirm that the quality of both the perovskite absorber and the metal oxides grown on PCBM are satisfactory to produce working devices.

Next, we discuss the results of ALD processing of both oxides directly on the perovskite absorber. XRD patterns in Fig. S5, Sec. V, in the supplementary material⁷³ show no indication of perovskite structure degradation, usually associated with the presence of lead halide crystalline peaks. Based on literature results (see Table I), we process 6 nm-thick metal oxides on top of the perovskite and evaluate the cell performance. Note that the deposition of thicker SnO_2 and TiO_2 films did not result in improvement in the device performance (Fig. S4, Sec. IV, in the supplementary material⁷³). The J-V curves for the cell structure reported in Fig. S2(c), Sec. III, in the supplementary material,⁷³ are shown in Fig. 2. Both cells show the presence of a large J-V hysteresis and reduced performance compared to that of the PCBM/metal oxide-based cells. In the case of SnO_2 , contributing to the poor performance, we also observe a strong s-shaped character in the J-V curves. The efficiency of cells with SnO_2 falls within the range of efficiencies reported in the literature.^{8,10} Nonetheless, a more detailed comparison of the obtained

FIG. 2. J-V curves of p-i-n perovskite solar cells with the configuration shown in Fig. S2(b), Sec. III, in the supplementary material (Ref. 73). PV parameters are reported in Table I.

results with literature data cannot be carried out due to the different halide ratios, nature of cations, and synthesis of the absorber.

For the case of 6 nm TiO_2 serving as the ETL, despite the large J-V hysteresis, we obtain a promising PCE of 13.6% (reverse scan) and 11% (deduced from MPPT) (MPPT in Fig. S3, Sec. IV, in the supplementary material⁷³). To the best of our knowledge, cells with only TiO_2 serving as an ETL have not been previously reported. The poor performance of SnO_2 , compared to TiO_2 , as the sole ETL might be caused by chemical changes taking place at the perovskite surface upon ALD processing and/or by the quality of the SnO_2 film in its initial growth stage. In addition, an unfavorable band alignment may develop between the perovskite and SnO_2 . We address these factors in Secs. III B and III C by combining XPS and UPS analyses carried out on the perovskite/metal oxide interface.

B. Chemical changes at the perovskite/metal oxide interface

In order to analyze the chemical changes occurring at the perovskite surface upon ALD processing of metal oxides, XPS is carried out on the pristine perovskite and on perovskite/metal oxide systems, for a wide range of metal oxide thicknesses (from 0.3 to above 10 nm). The thickness of the metal oxide layers is determined according to the procedure outlined in Sec. VI in the supplementary material⁷³ Table II and Table SII, Sec. VII, in the supplementary material⁷³ report the BE values for the features present in the perovskite and perovskite/metal oxide spectra, which are shown next. The left part of Table II reports the BE values for the pristine perovskite spectra, which are in agreement with other works.^{41,42} Next to these spectra, additional features (right part of Table II) appear when metal oxides are grown on perovskites,

TABLE II. Binding energy values of XPS spectral features for the pristine perovskite, perovskite/3 nm SnO_2 , and perovskite/3 nm TiO_2 .

XPS spectral feature	BE values of pristine perovskite (eV)	BE values of new features for	
		perovskite/ SnO_2 (eV)	perovskite/ TiO_2 (eV)
Br-3d _{5/2}	68.7	69.5	N/A
Br-3d _{3/2}	69.8	70.6	N/A
I-3d _{5/2}	619.5	620.5	N/A
I-3d _{3/2}	631.0	632.0	N/A
Pb-4f _{7/2}	138.7	139.3	
Pb-4f _{5/2}	143.6	144.2	
N-1s	400.8	Range of BE: 398.3–399.9	
Cs-3d _{5/2}	725.1	N/A	
Cs-3d _{3/2}	739.0	N/A	

pointing to the formation of new chemical states found for I, Br, Pb, and N spectra upon ALD processing.

Figures 3(a)–3(c) show the changes that the I-3d_{5/2} spectrum of the pristine perovskite undergoes upon 3 nm metal oxide deposition. Similarly, Figs. 4(a)–4(c) address the changes for the Br-3d spectrum. In the case of TiO_2 growth, no new features are detected [Figs. 3(b) and 4(b)]. Instead, as a result of the growth of SnO_2 , additional halogen-related contributions are detected at higher BE values than those associated with pristine perovskites [Figs. 3(a) and 4(a)]. Figures 3(d) and 3(e) and Figs. 4(d) and 4(e) show the trends of the peak area evolution of the halide species in the perovskite and of the newly formed species upon SnO_2 and TiO_2 growth, respectively.

The trend of the I-3d_{5/2} peak area related to pristine perovskite [Fig. 3(d)] follows the theoretical exponential decay due to the increasing thickness of metal oxide film atop. The exponential decay is described by Eq. S2 in Sec. V in the supplementary material.⁷³ This is expected for the iodine contribution in pristine perovskite since I-3d_{5/2} is selected for the determination of the metal oxide thickness, as discussed in Sec. VI in the supplementary material.⁷³ The trend of the perovskite-related Br-3d_{5/2} spectral area shows, instead, a deviation with respect to the theoretical exponential decay in Figs. 4(d) and 4(e). This suggests that, upon metal oxide deposition, there is an excess of perovskite-related Br^- species (with respect to I^-), which develops at the perovskite/metal oxide interface.

The newly formed species observed in Figs. 3(d) and 4(d) are found only in the case of SnO_2 . The observed initial rise suggests their formation, while the decay can be associated with the attenuation of the signal because of the increase in metal oxide thickness. Therefore, we can conclude that the new halogen-related species accumulate at the perovskite/ SnO_2 interface and are possibly embedded in the metal oxide film in its early growth stage. This accumulation of molecular halides is expected to lead to a resistive SnO_2 , therefore contributing to the observed s-shaped J-V curve in Fig. 2 for the PSC structure implementing SnO_2 as the ETL.

Halogen accumulation near the interface has been reported earlier in the literature, in the case of $(\text{FA},\text{MA})\text{Pb}(\text{I},\text{Br})_3/\text{SnO}_2$ using XPS depth profiling. However, no identification of new chemical states has been discussed so far.⁸ The BE values observed

FIG. 3. I-3d_{5/2} spectra for (a) perovskite/3 nm SnO₂, (b) perovskite/3 nm TiO₂, and (c) pristine perovskite. Each spectrum is normalized to the peak intensity of the pristine perovskite. Intensity evolution of the I-3d_{5/2} peak for (d) perovskite/SnO₂ and (e) perovskite/TiO₂. In (d) and (e), dashed lines show the attenuation of the I-3d_{5/2} signal upon metal oxide deposition on the perovskite.

FIG. 4. Br-3d_{5/2} spectrum for (a) perovskite/3 nm SnO₂, (b) perovskite/3 nm TiO₂, (c) and pristine perovskite. Each spectrum is normalized to the peak intensity of the pristine perovskite. Intensity evolution of Br-3d_{5/2} for (d) perovskite/SnO₂ and (e) perovskite/TiO₂. In (d) and (e), dashed lines show the theoretical attenuation of the Br-3d_{5/2} signal upon metal oxide deposition on the perovskite.

in our studies strongly suggest the formation of X_2 (where $X = \text{I}$ or Br),^{43–46} although X_3^- species and oxyhalides cannot be totally excluded.^{44,47,48} Instead, upon ALD of TiO_2 [Figs. 3(e) and 4(e)] as well as of Al_2O_3 (Fig. S11, Sec. VI, in the supplementary material⁷³), halogen species formation is not observed. It is also worth noting that the formation of I_2 and Br_2 at the interface occurs also for shorter exposure times of the perovskite to the TDMA-Sn precursor, as concluded from experiments on spatial-ALD (S-ALD) processing of SnO_2 , carried out under atmospheric pressure conditions (Fig. S12, Sec. VII, in the supplementary material⁷³).

When comparing the trends of I_2 and Br_2 as a function of the SnO_2 thickness [Figs. 3(d) and 4(d)], it can be observed that the Br_2 contribution is larger than the one associated with I_2 . The pristine perovskite is iodine-rich (i.e., the XPS I:Br ratio is 17:1) at the surface, whereas we detect an I_2 : Br_2 ratio of 0.5:1 after SnO_2 processing (for all film thicknesses used). This observation indicates that a larger amount of bromine species is present at the perovskite/ SnO_2 interface.

Next, we discuss the changes occurring in the Pb-4f spectral feature upon metal oxide deposition, as shown in Figs. 5(a) and 5(b). We observe the development of a lead-containing species with a doublet at larger BE values than that of the Pb^{2+} doublet in pristine perovskite. The corresponding evolution of the peak area as a function of the metal oxide thickness related to Pb^{2+} perovskite species follows the theoretical trend, similar to the I^- perovskite species, suggesting that the Pb/I ratio at the perovskite interface does not change during the growth of the metal oxide films. The

trend of the peak area evolution of the newly formed Pb species [Figs. 5(d) and 5(e)] points out to its accumulation at the perovskite/metal oxide interface.

The BE values of the new Pb species do not correspond to PbO (Ref. 41) or metallic Pb.^{49,50} Instead, they point to the formation of PbX_2 species, which are decomposition products of the perovskite where Pb^{2+} holds the same oxidation state.^{51,52} The earlier addressed accumulation of Br^- species at the interface confirms the formation of lead halide, specifically PbBr_2 , upon the deposition of SnO_2 and TiO_2 , whereas no evidence of PbI_2 formation can be found from XPS. Since no trace of PbBr_2 (as well as PbI_2) is found in the XRD patterns (Fig. S5, Sec. V, in the supplementary material⁷³), we can indeed conclude that PbBr_2 formation is limited and confined to the perovskite surface and likely has an amorphous structure, making it undetectable by XRD. PbBr_2 formation is also observed for the perovskite/ Al_2O_3 system (Fig. S11, Sec. VI, in the supplementary material⁷³) and in the case of S-ALD processing (Fig. S12, Sec. VII, in the supplementary material⁷³). The observation of ultrathin PbBr_2 at the interface for iodine-rich perovskite has not been reported before, to the best of our knowledge. Its presence at the interface between the perovskite and the metal oxides can cause the accumulation of charge carriers, due to its resistive character. Charge accumulation is then held responsible for the hysteresis behavior observed in the J-V curves (Fig. 2).

The N-1s spectra and their evolution are presented in Figs. S10(a)–S10(c), Sec. VI, in the supplementary material.⁷³ The BE of the feature related to the FA cation of perovskite (400.8 eV)

FIG. 5. Pb-4f spectrum for (a) perovskite/3 nm SnO_2 , (b) perovskite/3 nm TiO_2 , and (c) pristine perovskite. Each spectrum is normalized to the peak intensity of the pristine perovskite. Note that the Sn-4s peak, not shown in Fig. 5(a), overlaps with the $\text{Pb-4f}_{7/2}$ peaks (it is broad and centered at 139.0 eV); it is however considered during the deconvolution of the Pb-4f spectrum. Peak intensity evolution of the two Pb-4f contributions for (d) perovskite/ SnO_2 and (e) perovskite/ TiO_2 . In (d) and (e), dashed lines show the theoretical attenuation of the $\text{Pb-4f}_{7/2}$ signal upon metal oxide deposition on the perovskite.

is present in both pristine perovskite and perovskite/metal oxide samples. The peak area attenuation follows the expected trend [Figs. S10(f)–S10(g), Sec. VI, in the supplementary material⁷³], just like the Pb^{2+} and I^- species of the pristine perovskite, suggesting that FA is not depleted from the interface under the processing conditions used in this work. In addition, both perovskite/metal oxide systems show new nitrogen peaks in the BE range of 398.3–399.9 eV. A contribution to these peaks derives from nitrogen species incorporated in the metal oxides due to the residual ligands of the metal precursor molecules TDMA-Sn and TDMA-Ti.^{53,54} This is observed also in the case of growth on c-Si substrates [Figs. S10(d)–S10(e), Sec. VI, in the supplementary material⁷³]. Another contribution in terms of new nitrogen species can arise from the chemical modification of the FA cation, as observed in the perovskite/ Al_2O_3 case, where a nitrogen-free ALD precursor is used [Fig. S11(b), Sec. VI, in the supplementary material⁷³]. Given the overlap between the two contributions in terms of BE values, we cannot exclude that the chemical modification of FA occurs upon deposition of TiO_2 and SnO_2 .

C. Chemical composition of metal oxide films and energetics of the perovskite/metal oxide interface

The oxygen-to-metal ratio (O:M) for both metal oxide films grown on perovskites is evaluated and reported in Fig. 6(a). As a reference, we observe that, when SnO_2 film is grown on PCBM, the O:M ratio is ~ 2 , regardless of the film thickness. Note that for the calculation of the stoichiometry of the metal oxides, only the chemical state belonging to the oxygen bonded to the metal is

considered. Other chemical states detected in the O-1s spectra and belonging to carbonaceous states like the $\text{C}=\text{O}$ bond or the $\text{C}-\text{O}$ bonds found in PCBM or to the $-\text{OH}$ groups present on the surface of the perovskite and on the metal oxides are excluded from the estimation of the O:M ratio. For the perovskite/ SnO_2 case, thin films are found to be significantly oxygen-deficient, while for SnO_2 thicknesses above 10 nm, the ratio increases toward 2. The substoichiometry in the initial stage of SnO_2 growth suggests the presence of both Sn^{4+} and Sn^{2+} states. Unfortunately, the BE values of these states cannot be resolved in the Sn-3d XPS spectrum.⁵⁵

Therefore, to determine the presence of defects in the metal oxide films, UPS measurements are carried out on films of different thicknesses deposited on top of the perovskite. For SnO_2 , we observe a contribution to the density of states (DOS), assigned to Sn^{2+} with the edge located 1.8 eV above the valence band maximum (VBM) shown in Fig. 6(b). Oxygen deficiency in SnO_2 is expected to give rise to localized occupied electronic states within the bandgap of SnO_2 located above the valence band maximum.^{56–59} They appear as a result of hybridization between Sn-4d, Sn-5s, and O-2p states, bear excitonic character, and are more pronounced in the case of amorphous SnO_2 films.^{60–62} In theoretical works,^{63,64} it was suggested that these Sn^{2+} states develop upon removal of oxygen from bridging positions. So far, they have been experimentally observed^{61,62} only upon ion bombardment or heating in ultrahigh vacuum conditions.

Furthermore, this subgap defect contribution is found to decrease with increasing SnO_2 thickness as reported in Fig. S13(a) A, Sec. VIII (please refer to the discussion on the deconvolution of defect DOS in Sec. VIII in the supplementary material).⁷³ Since

FIG. 6. (a) Oxygen-to-metal ratio, derived from XPS spectra, as a function of the metal oxide thickness for SnO_2 (grown on perovskite and PCBM) and TiO_2 . Only the contributions of oxygen peaks originating from O–Sn and O–Ti bonds are considered in these calculations; extra contributions from surface O–H or O–C species are excluded. (b) UPS valence band spectra of the 6 nm SnO_2 layer grown on the perovskite with fitted subgap density of states, as discussed in Sec. VIII in the supplementary material (Ref. 73).

UPS probes up to a depth of ~ 1 nm, this analysis reveals that the defects are located at the perovskite/ SnO_2 interface rather than on the surface of SnO_2 film in contrast to the literature observations mentioned above.

In the TiO_2 case [Fig. 6(a)], the O:M ratio is constant as a function of the film thickness and in the range of 1.8–1.9. Moreover, we do not observe Ti^{3+} states in the Ti-2p spectra [Fig. S8(h), Sec. VII, in the supplementary material⁷³]. Such states are reported to give rise to a subgap peak located below the E_f and 1 eV above the VBM of TiO_2 .^{65–68} In parallel, the UPS spectra of TiO_2 grown on perovskite [Fig. S13(b), Sec. VIII, in the supplementary material⁷³] do not show any evidence for Ti^{3+} states in the valence spectrum.

IV. DISCUSSION

The evidence of SnO_2 substoichiometry and the presence of subgap defect states located at the interface with the perovskite suggest that a redox reaction occurs at the early phase of SnO_2 growth due to the interaction of the metal precursor with the perovskite substrate. Specifically, we speculate that the Sn(IV) metal center is reduced to Sn(II), whereas halide (X^-) species, originating either from the perovskite itself or from its decomposition products (e.g., PbX_2 , HX , or FAX), are oxidized to X_2 (Br_2 and I_2). We exclude that a redox reaction involving the participation of halides and the Sn(IV) atoms in the metal oxide is taking place, since high temperatures would be required.⁶¹ Instead, we suggest that it is the metal center in the metalorganic precursor that interacts with the perovskite. As a result, an oxygen defective SnO_2 film containing Sn(II) states and embedded halogen molecules develops. Both chemical changes contribute to the resistive character of SnO_2 , which results in the s-shaped J-V curves for cells implementing SnO_2 ETL. Earlier [Figs. 3(a) and 4(a)], we referred to diatomic halogen formation at the perovskite/ SnO_2

interface, opposite to the case of the perovskite/ TiO_2 interface, where also substoichiometry is not observed. This difference strongly suggests that TDMA-Ti and TDMA-Sn precursors behave differently when chemisorbing on the perovskite. Most certainly, the difference in electronegativity between the two metal atoms plays a role.

Next, we evaluate the valence band alignment of the perovskite/metal oxide systems, using UPS. Specifically, we assess the charge selectivity of SnO_2 and TiO_2 by considering the presence of DOS related to defects in the case of SnO_2 . UPS is a widely adopted technique that provides information about energetics and band alignment in perovskite cells.⁶⁹ Using the values of E_f and VBM extracted from UPS measurements⁷⁰ (Fig. S14, Sec. VIII, in the supplementary material⁷³), we present the energy band diagram in Fig. 7 (under dark conditions) for the pristine perovskite and perovskite/6 nm-thick metal oxides. The energy levels are aligned to the E_f position, in order to unravel other potential interfacial effects, such as dipole formation. As a matter of fact, the formation of a dipole is observed for both systems, characterized by the shift of the vacuum level of 0.2 eV (for the SnO_2 case) and 0.4 eV (for the TiO_2 case). The presence of the dipole is supported by the observation of shifts in the BE values of the perovskite (Sec. II in the supplementary material⁷³) upon deposition of metal oxides and could contribute to the presence of hysteresis in the current-voltage characteristics of the cells (Fig. 2).

The subgap DOS related to the defect states, present at the perovskite/ SnO_2 interface, is schematically depicted in Fig. 7 as a probability density function in the region above the VBM of SnO_2 for the 6 nm film. The presence of the subgap defect states in thin SnO_2 films, which effectively broaden the VB, decreases the SnO_2 selectivity as an electron transport layer. The energetic alignment of the defect edge with the VBM of the perovskite will favor hole injection into the defect states of SnO_2 . Such defect states act as

FIG. 7. Energy level diagrams for the pristine perovskite (grown on ITO/PTAA) and upon deposition of 6 nm of (a) SnO_2 or (b) TiO_2 . The energy levels are aligned to E_f . The positions of the valence band maxima (VBM), vacuum levels, and the edge of subgap DOS for perovskite/ SnO_2 case are shown in the figure, whereas the conduction band minima are not reported.

hole traps⁵⁹ and contribute to increase hole-electron recombination processes at the perovskite/SnO₂ interface. Figure 7 does not include the conduction band minimum for SnO₂: it is experimentally complex to determine it for very thin metal oxides grown on perovskite. However, theoretical calculations⁵⁶ predict that the presence of oxygen vacancies within the SnO₂ give rise to unoccupied tail states below the CBM effectively reducing the bandgap of the material.⁵⁶ Such an observation would enhance the hole-electron recombination processes mentioned above. In conclusion, the poor cell performance reported in Fig. 2 is attributed to the loss of SnO₂ electron selectivity and recombination processes.

Instead, for the perovskite/TiO₂ interface, which lacks subgap states, the hole injection is impeded due to the favorable VBM offset between the perovskite and TiO₂ (2.5 eV). This observation aligns with the promising p-i-n cell efficiency when TiO₂ is adopted as the ETL.

V. SUMMARY AND CONCLUSIONS

This manuscript focuses on the factors limiting the perovskite solar cell efficiency when metal oxides processed by ALD are adopted as ETLs and grown directly on the perovskite absorber. To this purpose, we carry out a systematic and in-depth investigation of the chemical changes occurring at the interface between the perovskite and SnO₂ and TiO₂ and correlate them to the p-i-n cell performance.

The dual cation (Cs,FA)-based perovskite withstands ALD processing, since the bulk of the material remains unaltered upon the growth of the investigated metal oxides. For both metal oxides, we report the common interfacial changes related to the formation of a thin PbBr₂ layer and the formation of a dipole, based on XPS and UPS analyses. These changes may contribute to the observed large J-V hysteresis in both cases.

In the case of SnO₂ as the ETL, we observe a poor cell performance and strongly s-shaped J-V curves. We relate this result to the chemical changes directly affecting the electronic properties of SnO₂ metal oxide at the interface. These chemical changes are the formation of halogen molecules (Br₂ and I₂) and the presence of an oxygen deficiency of SnO₂ in the early phase of its growth. This substoichiometry is accompanied by the development of subgap states related to Sn²⁺ above the valence band maximum, which act as hole traps at the perovskite/SnO₂ interface, subsequently promoting charge recombination and negatively affecting the performance of the cell. The observed changes at the perovskite/SnO₂ interface have been attributed to a redox reaction between halide species (I⁻ and Br⁻) of the perovskite or its decomposition products and the Sn(IV) metal center of the TDMA-Sn precursor.

Instead, when adopting TiO₂ as the ETL, we report a promising device performance of 13.6% (MPPT 11%). In the case of TiO₂ processing, there is no evidence of redox processes between the halides and the Ti(IV) metal center during film growth. Consequently, the perovskite/TiO₂ interface exhibits no signature of subgap states and has a favorably large VBM offset. We also conclude that TiO₂ is a potentially more suitable ETL for p-i-n perovskite cells directly applied on top of the perovskite absorber without the need of an organic interlayer. However, in order to reduce the hysteresis in cells employing TiO₂ ETLs, the formation of PbBr₂ should be avoided or at least minimized and further

investigation on other perovskite compositions is required in order to tackle this problem. Concurrently, investigating the application of an ultrathin passivation layer, carrying a fixed positive charge, like the PO_x/Al₂O₃ bilayer,^{71,72} could be attempted to improve the charge selectivity of the interface between TiO₂ and the perovskite to reduce the hysteresis. The use of a TiO₂ ETL may then not only be more cost-effective but also more suitable for process upscaling.

Finally, the predominant formation of Br₂ at the perovskite/metal oxide interface suggests investigating a perovskite surface less prone to redox reactions with specific ALD precursors by tuning the halide composition. Moreover, further understanding of the interaction of ALD precursors with the metal halide perovskite, supported by density functional theory (DFT) calculations, is required in order to shed light on the preferential participation to the redox process of Br⁻ species and TDMA-Sn precursor, instead of TDMA-Ti.

As a concluding remark, we consider highly intriguing the fact that nowadays ALD research in perovskite PVs draws the attention of the PV perovskite community in ALD (and spatial-ALD). Therefore, next to control on parameters such as substrate temperature and processing time, we believe that this research field requires major efforts to generate insights into the surface reactions between the specific ALD chemistry and the chemically challenging nature of hybrid metal halide perovskite absorbers.

AUTHORS' CONTRIBUTIONS

A.E.A.B., C.H.B., and A.T. contributed equally to the work.

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To the 16 years old herself, she would say: “*Don’t be scared. Do what you would like and like what you do.*”