Strong Performance Enhancement in Lead-Halide Perovskite Solar Cells through Rapid, Atmospheric Deposition of *n*-type Buffer Layer Oxides

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**Abstract**

Thin (approximately 10 nm) oxide buffer layers grown over lead-halide perovskite device stacks are critical for protecting the perovskite against mechanical and environmental damage. However, the limited perovskite stability restricts the processing methods and temperatures (≤110 °C) that can be used to deposit the oxide overlayers, with the latter limiting the electronic properties of the oxides achievable. In this work, we demonstrate an alternative to existing methods that can grow pinhole-free TiO*x* (*x* ~ 2) films with the requisite thickness in <1 min without vacuum. This technique is atmospheric pressure chemical vapor deposition (AP-CVD). The rapid but soft deposition enables growth temperatures of ≥180 °C to be used to coat perovskites with or without a protective layer of PC61BM. This is ≥70 °C higher than achievable by current methods and results in more conductive TiO*x* films, boosting solar cell efficiencies by >2%. Likewise, when AP-CVD SnO*x* (*x* ~ 2) is grown directly on the perovskite, there is also minimal structural damage to the underlying perovskite layer. The SnO*x* layer is pinhole-free and conformal. When used to cover perovskite devices with a PC61BM electron transport layer, shunting due to the pinholes in the spin-coated PC61BM is reduced, resulting in increases in the steady-state efficiency from 16.5% (no SnO*x*) to 19.4% (60 nm SnO*x*), with fill factors reaching 84%. This work shows AP-CVD to be a versatile technique for growing oxides on thermally-sensitive materials.

1. Introduction

Lead-halide perovskites are attracting substantial attention for energy and optoelectronic applications, owing to rapidly rising efficiencies in devices, including photovoltaics [1], light-emitting diodes [2,3], X-ray detectors [4] and photodetectors [5]. These materials have the stoichiometry ABX3, in which A is a monovalent cation (*e.g.*, methylammonium or MA+), B a divalent cation (*i.e.*, Pb2+) and X a halide (*e.g.*, I-). As such, lead-halide perovskites are versatile materials with band gaps that can be tuned over the entire visible light range by changing the composition [6]. These materials exhibit an exceptional tolerance to point defects, *i.e.*, the lead-halide perovskites can achieve long charge-carrier lifetimes and high luminescence quantum yields, despite being grown from solution with high densities of vacancies and interstitials [7]. An important restriction, however, is the limited thermal, environmental and mechanical stability of lead-halide perovskites. MAPbI3, in particular, is thermodynamically unstable [8] and thin films have been reported to degrade in ambient air at room temperature within days [9]. Improved thermal stability has been achieved in ‘triple-cation’ perovskites, in which the MA+ is replaced with a mixture of Cs+, formamidinium (FA+) and MA+ [10]. However, the photovoltaic performance of triple-cation perovskites still decreases from 20% to 18% after 250 h continuous operation at room temperature in an inert nitrogen environment [10]. Similarly, the low mechanical stability of the perovskites results in films being damaged when bombarded by energetic particles, such as during sputter-deposition [11]. Recently, the use of compact oxides grown over the perovskite has led to significant improvements in stability. Although the oxides are deposited directly on the perovskite in some works [12], it is common for the perovskite to be directly interfaced with organic charge transport layers and the protective oxide grown over the organic layer [13–15] to achieve low rates of non-radiative recombination, efficient charge extraction and protect the perovskite from damage when depositing the oxide [16,17].

By depositing a 50 nm thick layer of Al-doped ZnO nanoparticles on perovskite/PC61BM in *p*-*i*-*n* structured solar cells, Bush *et al.* successfully protected the perovskite from mechanical damage when growing a transparent indium tin oxide (ITO) electrode on top by sputter-deposition. The resultant semi-transparent perovskite top-cells were used in four-terminal tandems with silicon [11]. However, the nanoparticle layer needed to be thick to be pinhole-free, leading to series resistance losses [11,15]. This limitation was subsequently overcome by using atomic layer deposition (ALD) to grow a pinhole-free, thin bilayer of 4 nm SnO*x* and 2 nm zinc tin oxide on perovskite/C60 [15]. ALD has also recently been used to grow a 18–40 nm thick layer of amorphous TiO2 over perovskite/PC61BM, which protected the perovskite for 2 h in acidic electrolytes, allowing them to be used as photocathodes for water splitting [18]. The ability of ALD to grow dense oxides has recently led to extensive work on the use of ALD Al2O3 passivation layers grown on perovskite solar cells, with many groups reporting an improvement in stability through the use of a thin Al2O3 barrier layer against moisture penetration [19–26]. This mirrors the increasing use of ALD Al2O3 as passivation layers in commercial silicon solar cells [27], particularly since industrial-scale ALD reactors are now capable of depositing Al2O3 onto 800 wafers per batch, enabling a reported throughput of 3600 wafers per hour [28]. However, ALD is inherently limited by a low growth per cycle due to long purge times being required between precursor exposure steps [19,21,22,29]. Although ~1 nm Al2O3 layers can still be deposited within minutes, thicker active layers (*e.g.*, of TiO2 or SnO2) require processing times >30 min per batch [18,30,31]. Such long processing times can lead to thermally-induced damage to the perovskite [30]. Moreover, some organometallic precursors, such as trimethylaluminium (for Al2O3) and diethylzinc (for ZnO), can damage the surface of the perovskite [29,32]. Sputter-deposition is a commercially-available alternative to ALD that has a significantly higher growth rate, but the high kinetic energy of the particles involved in the deposition would also typically damage the perovskite [11,15]. A recent work showed that perovskites with sputtered ZnO buffer layers were less efficient than similar devices with spin-coated ZnO nanoparticle buffer layers (12.5% *vs*. 16.1% respectively) [33].

Although a wide range of deposition methods and processing conditions can be used to grow oxide charge transport layers beneath the perovskite, only a small selection of these methods and a narrow range of growth temperatures have been shown to be compatible with growing oxides on top of the perovskite, even when it is covered with an organic layer. Apart from spin-coating colloidal nanocrystals, ALD and sputter-deposition, thermal evaporation has also been used, but mainly for high work function *n*-type oxides to extract holes rather than low work function oxides for extracting electrons. In order to manufacture oxide buffer layers on a large scale for device applications (*e.g.*, top-cells or photocathodes), the growth technique should: 1) yield conductive oxides without damaging the perovskite, 2) result in pinhole-free and dense films, 3) feature rapid but uniform film growth, 4) be scalable, and 5) produce films that are conformal to textured substrates. The latter is particularly important for applications in tandem solar cells with silicon, in which the highest efficiencies have been achieved with front-textured silicon, requiring conformal perovskite, charge transport and oxide buffer layers [34,35]. However, the current techniques used for growing oxide buffer layers are not able to achieve all requirements simultaneously (Table 1). Whilst dense, conformal and uniform oxide films can be achieved by ALD and thermal evaporation, both techniques are vacuum-based methods with a low growth rate or growth per cycle. By contrast, spin-coating oxide nanoparticles is a fast and facile method on a lab-scale without requiring vacuum, but is not conformal and is challenging to scale-up to the module-level. A particular challenge with all growth methods is that the thermal instability of the lead-halide perovskite limits the maximum processing temperature which can be used for the deposition of oxides over perovskite films, even when they are covered with a fullerene electron transport layer. For example, Palmstrom *et al.* found that cesium-formamidinium-based perovskites (more thermally-stable than MAPbI3) had bulk structural degradation when ALD SnO2 was deposited at 110 °C or above [30]. This degradation occurred regardless of whether the perovskite was first covered with the 1 nm LiF/10 nm C60 electron transport layer [30]. As shown in Table S1, SI, oxides grown by any of the current techniques have typically been processed at up to 100 °C, and in many cases at room temperature. But this limits the electronic properties of the oxides achievable, since higher mobilities and, presumably in some cases, improved band alignment of the oxide with the perovskite is achieved at higher deposition or annealing temperatures [36–38]. Variants of ALD have also been proposed that can grow pinhole-free and conformal oxides more rapidly. These are pulsed chemical vapor deposition (pulsed-CVD, in which the purge times in ALD are reduced) [30] and spatial atomic layer deposition (in which the metal precursor and oxidant are spatially-separated) [39–41]. However, Palmstrom *et al.* found that cesium-formamidinium-based perovskites (with and without a LiF/C60 electron transport layer) still degrade when depositing SnO2 buffer layers at 110 °C or above by pulsed-CVD [30]. Riedl *et al.* found that when increasing the temperature for growing SnO2 on MAPbI3/PC61BM/Al:ZnO NP stacks by spatial ALD to above 80 °C, there was still a decrease in the solar cell efficiency [14]. These methods are therefore not suited to overcome the challenges of the current techniques for growing oxide buffer layers for perovskite devices.

**Table 1.** Summary of the key requirements for growing oxide buffer layers on lead-halide perovskite device stacks and how much each oxide growth method fulfils each requirementa

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Deposition method/Requirement | Wide processing windowb | Pinhole-free | Fast growth | Scalable | Conformal |
| Spin-coating oxide nanoparticles | 🗴 | – | 🗸 | 🗴 | 🗴 |
| Atomic layer deposition | 🗴 | 🗸 | – | 🗸 | 🗸 |
| Sputter deposition | 🗴 | 🗸 | 🗸 | 🗸 | 🗸 |
| Thermal evaporation | 🗴 | 🗸 | – | – | 🗸 |
| AP-CVD (this work) | 🗸 | 🗸 | 🗸 | 🗸 | 🗸 |

a ‘–’ signifies partial fulfilment

b Processing window captures the range of deposition temperatures compatible with growing on perovskites, range of oxidants that can be used, extent to which the deposition method damages the perovskite and ultimately the efficiencies that can be achieved

An unexplored alternative for oxide film growth over iodide-based perovskites is atmospheric pressure chemical vapor deposition (AP-CVD). AP-CVD uses the same precursors as ALD, but mixes them in the gas phase to obtain CVD rather than self-limiting growth (Figure 1a). Thus, AP-CVD has higher growth rates per unit time and per cycle than spatial ALD [39,42]. Also, AP-CVD processes oxides under ambient conditions without a vacuum chamber and is compatible with high-throughput roll-to-roll manufacturing, unlike pulsed-CVD[30,39,42]. We previously developed a gas manifold (Vertical Cambridge University Close Proximity reactor, or V-CUCP) that distributes the gas precursors uniformly across the manifold and guides the gases vertically down to the substrate held tens of μm below (Figure 1a). This reactor is described in detail in Ref. [42], which includes schematics of the setup. In brief, the metal precursor is introduced to the central channel in a gas manifold. The gas-phase oxidant is also introduced into two channels on either side of the metal precursor channel. These channels run parallel to each other. In between the oxidant and metal precursor gas channels, there are extra gas channels to which an inert gas (Ar in this case) is introduced. All of these gas channels guide the precursor or inert gases vertically down to the substrate, which is parallel to the bottom of the manifold and held by a platen (Figure 1a). The substrate-manifold spacing is manually adjusted, and varies from 50 m to 125 m. The platen heats the substrate to the reaction temperature and moves the substrate through all of the gas channels repeatedly, such that a uniform thin film is grown. The width of the film is set by the width of the gas manifold, and the length determined by the distance travelled by the platen. ZnO films grown by AP-CVD using the V-CUCP reactor were deposited at similar temperatures as ALD, with comparable thickness uniformity[39,42], conformality to high-aspect ratio nanowires[43], and with growth rates of 1.1 nm s-1, which was an order of magnitude larger than by ALD. Although AP-CVD has the potential to fulfil the film quality, growth rate, scalability and conformality requirements for manufacturing oxide buffer layers, a key question is whether the shorter deposition times achievable can allow higher deposition temperatures to be used without damaging the perovskite beneath the fullerene electron transport layer in a device stack, and whether this can lead to increased device performance. Furthermore, we have previously only demonstrated the growth of ZnO and Zn1-*x*Mg*x*O on MAPbBr3 for light-emitting diodes [44]. However, ZnO is known to degrade iodide-based perovskites (*e.g.*, MAPbI3) due to the high isoelectric point [45,46], and groups have reported that the diethylzinc precursor itself may react with the perovskite [32]. It is therefore important to determine whether AP-CVD can grow alternative oxides that are chemically inert to iodide-based perovskites suitable for solar cells, and whether AP-CVD can then overcome the limitations of the current methods for growing oxide overlayers on lead-halide perovskites.

In this work, we aim to understand whether AP-CVD can be used to broaden the processing window of *n*-type oxides grown over lead-halide perovskites, both bare films and perovskites covered with a complete layer of PC61BM for use in *p*-*i*-*n* structured solar cells. For the *n*-type oxides, we investigate TiO*x* and SnO*x*, grown by AP-CVD over the perovskite stacks for the first time, and compare with ZnO. We investigate the properties of the oxides grown, and compare their deposition on perovskite solar cells based on thermally-sensitive MAPbI3 and the more thermally-stable triple-cation perovskites (Cs0.05(MA0.17FA0.83)0.95Pb(I0.84Br0.16)3). For all oxide films, we compare the oxide growth at 100 °C with O2 gas oxidant *vs.* 150 °C with H2O vapor oxidant. In this work, we refer to these as *mild* and *strong* growth conditions respectively. We then investigate the impact of the oxide films formed under these two conditions on the performance of perovskite solar cells. Both the mild and strong growth conditions are typically inaccessible when using ALD to grow oxides over perovskites, either because chemisorption is not possible (mild conditions) [47], or because the perovskite would degrade (strong conditions). Strong growth conditions are also not accessible by solution-processing, thermal evaporation or sputter-deposition for growing oxide buffer layers on perovskites.

2. Results and Discussion

2.1. TiO*x* Overlayers

*2.1.1. AP-CVD TiOx Film Properties*

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**Figure 1.** (a) Illustration of growing oxides on lead-halide perovskite films by AP-CVD. Metal precursor vapor (M), oxidant (Ox) and inert gas (I, in this case Ar) are introduced to the gas manifold from both sides (cross-section of manifold shown), where they are guided vertically down to the substrate. The metal precursor and oxidant mix in the gas phase, and the oxide thin film is grown by chemical vapor deposition. The oxide thickness depends on the number of times the substrate is moved through the gas channels. In each AP-CVD cycle, the substrate moves through the metal precursor channel twice. The oxide is grown by a soft chemical-based method (unlike sputter-deposition), and the growth rates are high with no vacuum required (unlike ALD and thermal evaporation). Properties of AP-CVD TiO*x* grown onto MAPbI3. (b) Thickness of TiO*x* against exposure time per AP-CVD cycle, (c) thickness against total deposition time. Morphology, measured by atomic force microscopy, of (d) MAPbI3 thin film deposited on glass and (e) a sister sample with TiO*x* grown directly on top at 150 °C using H2O vapor as the oxidant. The root mean square roughness for both samples was 14 nm. Photographs of the samples measured are inset.

We began by focusing on TiO*x*. By varying the exposure time per cycle in our V-CUCP reactor from 27 ms to 800 ms, we found the growth regime to be CVD rather than ALD based on the linear dependence of the film thickness on exposure time, with no evidence of saturation being reached (Figure 1b; in ALD, the Ti precursor pulse times are typically 100-150 ms) [18,26]. Under mild processing conditions, the growth rate was 0.63±0.03 nm s-1, while under strong processing conditions, the growth rate was 1.19±0.04 nm s-1 (Figure 1c). The growth rates per AP-CVD cycle are shown in Figure S1, SI. The growth rates achieved by AP-CVD for TiO*x* are over two orders of magnitude larger than TiO*x* grown by ALD at comparable temperatures [48]. Our X-ray photoemission spectroscopy (XPS) measurements of the TiO*x* films (Figure S2, SI) had no distinct Cl 2*p* core level peak, indicating a high reaction yield of the TiCl4 precursor, with insignificant Cl incorporation in the resulting TiO*x* films. From XPS measurements of TiO*x* grown on MAPbI3/PC61BM and MAPbI3, we found the *x* values to be ~2 under mild and strong conditions (Figure S3&S4, SI and Table S2, SI). X-ray diffraction measurements showed the films to be amorphous (Figure S5, SI), which is consistent with ALD films grown at comparable temperatures [31]. The refractive indices of the TiO*x* films were 2.2 (mild conditions) and 2.3 (strong conditions) at 640 nm wavelength (Figure S6a, SI), which are comparable to the refractive indices of TiO2 grown by ALD under fully-saturated conditions at similar temperatures [31,49]. We found no measurable sub-bandgap states in the AP-CVD TiO*x* films and the Urbach energies were comparable (28 meV for mild conditions; 26 meV for strong conditions). Given that the O/Ti ratios were ~2, there is no evidence for large quantities of impurities or defects, and the increase in refractive index indicates an increase in the density of the films, which is consistent with previous work on ALD TiO2 [31,49]. These results indicate that AP-CVD TiO*x* was dense and compact, with the films grown under strong conditions being slightly denser. In addition, atomic force microscopy measurements showed the films to be free from pinholes (Figure S7, SI).

***2.1.2. Understanding whether Depositing TiOx on MAPbI3 or MAPbI3/PC61BM leads to Bulk or Surface Damage***

To understand whether the growth of AP-CVD TiO*x* over perovskites leads to damage, we used strong processing conditions (150 °C, H2O vapor) to grow over the most unstable perovskite (MAPbI3), giving us a ‘worst-case scenario’. After we grew 5 AP-CVD cycles of TiO*x* (7 nm film thickness, as determined from Figure S1, SI) directly over MAPbI3 thin films, there was no noticeable visual change in the film appearance or morphology, as measured by atomic force microscopy (Figure 1d,e). This suggests that the rapid growth of TiO*x* avoided the degradation of thermally-sensitive MAPbI3. This contrasts to previous reports for ALD TiO*x*, in which a 50 nm thick PC61BM layer was required over MAPbI3 to avoid bulk degradation when growing TiO*x* on top by ALD, due to the much longer total deposition time of approximately 1 h [50]. To show the importance of minimizing the exposure time to high deposition temperatures, we loaded MAPbI3 into a furnace with flowing Ar gas at 150 °C. 7 nm TiO*x* would take at least 70 cycles in ALD, and each cycle takes ~30 s [18,26,31]. We therefore kept the perovskite films in the furnace for 35 min and found the films to have bulk degradation, which occurred even when the perovskites were pre-coated with a dense layer of AP-CVD TiO*x* (Figure S8, SI). The level of degradation we found here is likely to be a lower limit on the degradation from ALD, in which the samples are also periodically exposed to vacuum as well.

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**Figure 2.** Analysis of the effect of depositing TiO*x* by AP-CVD directly on MAPbI3 thin films. (a) Diffraction patterns and (b) time-resolved photoluminescence (PL) of MAPbI3 with TiO*x* grown on top. \* denotes the position of where the PbI2 (001) diffraction peak would be. The time-resolved PL measurements were taken using an excitation wavelength of 400 nm and fluence of 0.2 mJ cm-2 pulse-1. The substrate for the diffraction and PL measurements was glass. X-ray photoemission spectra of (c) O 1*s*, (d) N 1*s*, (e) Pb 4*f* and (f) I 3*d* core level regions for MAPbI3 thin films compared to corresponding samples with TiO*x* (5 AP-CVD cycles) grown on top. Please note that the O 1*s* peak for MAPbI3 has been scaled based on its absolute intensity relative to the samples coated with TiO*x* due to its raw intensity being significantly lower. The legend for parts c) – f) are the same. The substrate for the X-ray photoemission spectroscopy measurements was glass/ITO/NiO*x*.

We next focused on the structural and optoelectronic properties of MAPbI3 films after the growth of the AP-CVD TiO*x* overlayer. After depositing 5 AP-CVD cycles of TiO*x* under mild and strong conditions directly on MAPbI3, the films remained phase-pure with no PbI2 peaks appearing (Figure 2a; close-up in Figure S9, SI). This shows there to be no bulk degradation, which again contrasts with ALD TiO2 grown directly on MAPbI3. We also observed no significant quenching of the photoluminescence (PL) lifetime when TiO*x* was grown by AP-CVD over MAPbI3 under strong processing conditions (Figure 2b). These suggest that no extra non-radiative recombination pathways were introduced by AP-CVD growth. However, we note that this does not exclude the possibility of degradation on the perovskite surface, since PbI2-based surface species can lead to improvements in lifetime and luminescence quantum efficiency [51].

To evaluate the effect of AP-CVD growth on the surface of MAPbI3, we performed X-ray photoemission spectroscopy (XPS) measurements (*hν* = 1486.6 eV). The TiO*x* layers were 7 nm or thinner, which allowed us to probe the buried perovskite/oxide interface. The survey spectra are shown in Figure S10, SI. In Figure 2c–f, the O 1*s*, N 1*s*, Pb 4*f* and I 3*d* core level peaks are compared, while the fits to these are shown in Figure S11, SI. The bare MAPbI3 film has a weak O 1*s* peak centered at 532.1±0.1 eV, which we attribute to adventitious oxygen. Following the deposition of the TiO*x* overlayers, another O 1*s* core peak centered at a binding energy of 530.7±0.1 eV appeared (Figure 2c & Figure S3b&c, SI). This has been attributed to oxygen bonded to titanium [52]. All samples show a N 1*s* peak centered at 402.5±0.1 eV, which is consistent with nitrogen present in methylammonium [53]. But after TiO*x* deposition, a second peak centered at 400.0±0.1 eV appeared, which is associated with N bonded in decomposition products from methylammonium [53], suggesting that the methylammonium cation was damaged following oxide deposition.

To evaluate whether the inorganic lattice of MAPbI3 was damaged, we compared the Pb 4*f* and I 3*d* core levels. We found no metallic Pb0 core peaks following oxide deposition. However, we found from fitting that there were new peak components centered at 138.9±0.1 eV (for Pb 4*f*7/2) and 619.1±0.1 eV (I 3*d*5/2). Both can be attributed to degradation products [21,53]. This suggests that iodine may have been removed from the MAPbI3 surface, leading to the formation of PbI2. This loss in iodine is usually accompanied by a concomitant loss in nitrogen, which is not observed here, as seen by the slight increase in the N/Pb ratio after TiO*x* deposition (Table 2) [24,53]. We note that an alternative explanation for the peak positions of the Pb 4*f* and I 3*d* core levels shifting to lower binding energies after oxide deposition (Figure 2e&f) is a change in band bending at the buried perovskite interface compared to the free surface. In this case, the damaged perovskite interface would exhibit a slight upward band bending, which would be detrimental for electron extraction. This notion is further supported by a very small shift in the valence band onset to slightly lower binding energies (Figure S10b, SI). Overall, our results from Figure 2 show that while the bulk of MAPbI3 was unaffected after depositing AP-CVD TiO*x* on top, the surface was damaged due to the sensitive nature of the perovskite.

**Table 2.** Ratio of elements in MAPbI3 films measured by X-ray photoemission spectroscopy

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Ratio | No Oxide | With TiO*x* | |
|  | 100 °C, O2 gas | 150 °C, H2O vapor |
| Without PC61BM | N/Pb | 1.6±0.1 | 2.2±0.1 | 1.8±0.1 |
| I/Pb | 6.0±0.1 | 2.5±0.1 | 2.9±0.1 |
| With PC61BM | N/Pb | 1.1±0.1 | 1.3±0.1 | 1.1±0.1 |
| I/Pb | 3.1±0.1 | 2.7±0.1 | 2.7±0.1 |

By quantifying the N/Pb and I/Pb ratios, we found that the as-deposited MAPbI3 was rich in methylammonium and iodine (Table 2). It is possible that the films were terminated with methylammonium iodide, with the iodide arranged at the top surface layer. But after depositing PC61BM, the N/Pb and I/Pb ratios became very close to stoichiometric (Table 2). This may be due to the chlorobenzene solvent used when spin-coating PC61BM washing away the excess methylammonium iodide on the perovskite surface.

The set of sister samples, comprised of MAPbI3 coated with a thin layer of PC61BM, was prepared in order to evaluate the effect of using a thin organic electron transport layer for protecting the underlying perovskite film during oxide deposition. In a similar approach, we were previously able to inhibit a chemical reaction between MAPbI3 and the MoO*x* layer grown on top by introducing a thin protective layer of spiro-OMeTAD in between [54]. The nominal average thickness of the PC61BM we used here was 5 nm, as determined by atomic force microscopy (AFM) measurements of PC61BM films deposited onto silicon. AFM measurements of the PC61BM-covered MAPbI3 samples reveal a non-uniform coating (Figure S12, SI), which indicates that areas of the PC61BM layer are significantly thinner than the average thickness. Pinholes in the PC61BM on both a nanometer and micron scale may also be present that could lead to the exposure of the underlying perovskite film (Figure S12, SI). This is likely due to the spin-cast PC61BM filling low-lying regions, leading to the higher areas being exposed or covered only with a monolayer of the fullerene [55]. As a result, we were able to measure the core levels from the buried perovskite interface by XPS (Figure S13, SI). These measurements showed that there was no change in the N 1*s*, Pb 4*f* and I 3*d* core level peaks of the MAPbI3 coated with PC61BM after depositing TiO*x* under either mild or strong conditions. No new peaks or peak components due to degradation products appeared after oxide deposition, and the I/Pb ratio remained within the ‘defect-tolerant’ range for MAPbI3 (Table 2) [53]. The apparent binding energy of the core level peaks also did not shift, indicating that no surface band bending occurred. Thus, employing the thin PC61BM layer mitigates the creation of any degraded perovskite interfaces during oxide growth. In addition, there was also no bulk degradation or quenching of the PL after oxide deposition (Figure S13a&b, SI). These results demonstrate that the rapid nature of oxide growth by AP-CVD enables minimal damage to the buried perovskite surface to be achieved, as well as avoiding damage to the perovskite bulk.

***2.1.3.* *Effect of AP-CVD TiOx Overlayers on Perovskite Device Performance***

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**Figure 3.** (a) Device structure used. The AP-CVD oxide here was TiO*x*. (b) Diffraction pattern of MAPbI3 after TiO*x* was deposited directly on top with 5 AP-CVD cycles using H2O vapor as the oxidant. \* denotes where the PbI2 (001) peak would be located if present. Power conversion efficiency of (c) MAPbI3 and (d) triple-cation perovskite solar cells as a function of the temperature of the platen the samples were mounted on when depositing an overlayer of TiO*x* by AP-CVD. The triple-cation perovskite was Cs0.05(MA0.17FA0.83)0.95Pb(I0.84Br0.16)3. The blue points are for cells with TiO*x* grown under strong conditions. The red point is for cells with TiO*x* grown under mild conditions. These are compared to cells with no oxide overlayer (control). In each case, the performance of six samples was averaged. The error bars each represent two standard errors.

To determine the effect of the TiO*x* growth conditions on the performance of MAPbI3 solar cells, we fabricated devices using a *p*-*i*-*n* structure (Figure 3a), with solution-processed NiO*x* as the hole transport layer and 40 nm thick PC61BM as the electron transport layer (as detailed in Section 4). It was necessary for the PC61BM layer to be sufficiently thick in order to fully cover the perovskite to both protect the perovskite surface from damage, as well as present a more suitable interface with the perovskite for efficient electron extraction. Therefore, whereas 5 nm PC61BM is ideal for photoemission spectroscopy measurements, it is not suitable for devices (refer to Table S3 and Figure S14, SI). We used bathocuproine (BCP) and Ag for the top electrode, in which the BCP acted as an interface modifier to ensure no barrier to electron extraction. The role of BCP in reducing the contact barrier for electron extraction from the high work function Ag top electrode has been well-documented [56,57]. Devices with a TiO*x* overlayer grown under mild conditions not only showed no decrease in performance compared to the control, but rather gave an improvement in efficiency (Figure 3b). Similarly, devices with TiO*x* grown under strong conditions gave more efficient devices than the control. We then kept the oxidant used to H2O vapor and varied the TiO*x* growth temperature from 60 °C to 200 °C. Surprisingly, we found that there was no significant decrease in the power conversion efficiency compared to the control until the growth temperature was 180 °C (Figure 3c). This is significantly higher than the perovskite-compatible growth temperatures reported for solution processing, ALD or sputter-deposition, in which the oxide layers could only be processed at up to 110 °C (Table S1, SI). We found that the range of perovskite-compatible growth temperatures was larger for triple-cation perovskites. With these samples, the power conversion efficiencies did not significantly decrease until the growth temperature was above 180 °C (Figure 3d). Even for the triple-cation perovskite devices with TiO*x* grown at 220 °C, there were some devices that were more efficient than the control (Figure S15, SI). This suggests that despite such elevated processing temperatures, not all of the perovskite device was degraded, which contrasts with perovskite devices that have solution-processed, sputter-deposited or ALD overlayers [30,50].

More surprisingly, we found that we could deposit TiO*x* directly onto the more thermally-sensitive MAPbI3 perovskite without inducing any bulk damage at deposition temperatures up to 200 °C (Figure 3b). However, the devices with TiO*x* grown at 180 °C or higher temperatures had larger series resistance and lower fill factors. This decrease in device performance may be due to changes to the buried perovskite interface beneath the PC61BM layer.

Our most efficient devices were triple-cation perovskites that had TiO*x* grown at 150 °C using H2O vapor as the oxidant (Figure 3b&c). When we replaced the BCP/Ag top electrodes with more reflective Al electrodes to obtain a more efficient control device (15.9% power conversion efficiency), adding a TiO*x* layer grown under strong conditions improved the performance to 17.1% (details in Figure S16 and Table S4, SI). The improvement in performance over the control was primarily due to an increase in the shunt resistance from 3000±1000 Ω cm2 (control) to 4000±3000 Ω cm2 (with TiO*x*), which correlated with increases in the fill factor from 70±3% to 76.4±0.3%. This is likely due to the spin-coated PC61BM layer being non-compact (Figure S17, SI) and the dense AP-CVD TiO*x* forming a pinhole-free layer covering it, thereby reducing shunt pathways.

***2.1.4.* *Understanding how TiOx Deposition Temperature affects Device Performance***

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**Figure 4.** Resistivity of TiO*x* grown at different temperatures using H2O vapor as the oxidant.

Growing TiO*x* at 150 °C led to more efficient device performance compared to other growth temperatures (Figure 3c&d). We hypothesized that the improvement in device performance when increasing the TiO*x* deposition temperature to 150 °C was due to a reduction in the resistivity of the oxide films. To test this, we grew 300 nm thick AP-CVD TiO*x* on ITO and evaporated Al on top. We measured the current density against applied bias and fitted the linear regime to calculate the resistivity (refer to Figure S18, SI for representative measurements). From these measurements, we found that the resistivity decreased from (4.7±0.8) × 104  cm (100 °C) to (1.7±0.2) × 103 Ω cm (150 °C), as shown in Figure 4. This correlated with a decrease in the series resistance of the MAPbI3 solar cells from 3.9±0.6  cm2 (100 °C) to 2.2±0.2  cm2 (150 °C), and an increase in the fill factor from 56±1% (100 °C) to 74±1% (150 °C). Similar trends were observed with the triple-cation perovskite devices. We were not able to determine the carrier properties of the AP-CVD TiO*x* films because the current – voltage curves did not consistently enter into the space-charge regime. But previous calculations and measurements on amorphous TiO2 showed the mobility to range from 10-4 cm2 V-1 s-1 to 0.1 cm2 V-1 s-1 [58,59]. Nevertheless, our resistivity measurements (Figure 4) show the importance of being able to open-up the processing window for TiO*x* in order to achieve higher-performing devices.

We note that TiO*x* films grown at 100 °C using O2 gas as the oxidant have similar resistivity ((4±3) × 104 Ω cm) as the films grown using H2O vapor at 100 °C ((4.7±0.8) × 104 Ω cm). However, in both MAPbI3 and triple-cation perovskite devices, the series resistance of the devices with TiO*x* grown with O2 gas was lower than those with H2O vapor. This was likely because the TiO*x* films grown with O2 were approximately half the thickness of the films grown with H2O vapor, due to the lower growth rate (Figure 1b), since the same number of AP-CVD cycles were used. Nevertheless, growing TiO*x* under strong conditions (150 °C, H2O vapor oxidant) would still lead to a lower contribution to the series resistance of the device than TiO*x* grown under mild conditions, since the resistivity for TiO*x* grown under strong conditions is an order of magnitude smaller (Figure 4).

2.2. ZnO and SnO*x* Overlayers

***2.2.1.* *Film Properties***

To determine whether AP-CVD can be more generally applied to enable other *n*-type oxides to be grown over perovskites across a wider processing window, we investigated ZnO and SnO*x*. We have previously shown that ZnO deposited with our V-CUCP reactor is grown under CVD mode with a growth rate of 1.1 nm s-1 [42], and films grown under strong conditions have a mobility of 5.5 cm2 V-1 s-1 and carrier concentration of 2  × 1019 cm-3 [60]. Whilst we have not measured the carrier properties of ZnO grown under mild conditions, we previously found that ZnO grown at 60 °C using O2 gas as the oxidant had four times higher resistivity than ZnO grown under strong conditions [44].

We investigated the growth regime of SnO*x* and found it to also be CVD from the linear relationship between film thickness and exposure time (Figure S20a, SI). The growth rates were 0.41±0.04 nm s-1 (mild growth conditions) and 0.27±0.02 nm s-1 (strong growth conditions), as shown in Figure S20b, SI. These growth rates were two orders of magnitude larger than literature reports for ALD SnO2 grown at 80 °C [14] or 100 °C [30], as well as being an order of magnitude higher than pulsed-CVD [30]. The films grown were amorphous (Figure S21, SI), and the refractive indices were 1.8 at a wavelength of 632 nm under both growth conditions (Figure S22a, SI), which is similar to previous reports of dense ALD SnO2 films grown at similar temperatures [38,61–63]. We note that the refractive index could be increased if SnO is present. But we checked the absorptance of 250 nm thick SnO*x* and found no sub-bandgap features in SnO*x* grown under mild conditions, while SnO*x* grown under strong conditions had only a small sub-bandgap feature (Figure S22, SI). We also found the valence band spectra of both films to more closely resemble SnO2 rather than SnO (Figure S23, SI). Thus, our refractive index measurements indicate that our AP-CVD films have similar density as ALD SnO2 films grown at similar temperatures [61,62]. Whilst we were not able to extract the carrier properties of these films from current–voltage measurements, we determined the resistivity to be on the order of 102 W cm, which is in the range of values reported for ALD SnO2 grown with the same Sn precursor under similar conditions [38,61]. Atomic force microscopy measurements of our AP-CVD films showed them to be free from pinholes (Figure S24, SI). The AP-CVD SnO*x* films were uniform over the measured 6.25 cm2 deposition area, with the thickness varying by only 1% (two standard errors compared to the average thickness), as shown in Figure S25, SI. From X-ray photoemission spectroscopy measurements, we found the *x* value for SnO*x* grown under both mild and strong conditions to be 1.98±0.07 (Figure S26&S27, SI). We previously found that AP-CVD ZnO grown in the same reactor has a thickness variation of only 3% over the entire deposition area [42].

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**Figure 5.** Growth of AP-CVD ZnO and SnO*x* on MAPbI3 and triple-cation (TC) perovskite. The TC perovskite was Cs0.05(MA0.17FA0.83)0.95Pb(I0.84Br0.16)3. X-ray diffraction patterns of as-deposited perovskite films compared to films that have (a) ZnO or (b) SnO*x* overlayers grown at 100 °C with O2 gas as the oxidant. Performance of (c) MAPbI3 or (d) TC solar cells with oxide overlayers. The device structure was glass/ITO/NiO*x*/perovskite/(40 nm) PC61BM/oxide/Al. (e) Illuminated and (f) dark current-density *vs.* voltage curves and (inset) steady-state power output of triple-cation PVs with AP-CVD SnO*x*.

***2.2.2.* *Understanding whether Depositing ZnO or SnOx onto Lead-Halide Perovskites by AP-CVD leads to Bulk Degradation***

We grew 100 AP-CVD cycles of ZnO and SnO*x* (2 min total deposition time) directly onto MAPbI3 and triple-cation perovskite films. The control triple-cation perovskite films without oxide overlayers have a small quantity of residual PbI2, which has been commonly observed in previous works [30,64,65]. The growth of the ZnO overlayers under mild conditions resulted in a higher relative intensity of the PbI2 peak for both MAPbI3 and triple-cation perovskite films (Figure 5a, Figure S28a&b, SI and Figure S29a&b, SI). This may have been due to ZnO itself degrading the perovskite due to its high isoelectric point or the diethylzinc precursor reacting with the perovskite surface, as discussed in previous reports [45,46]. But with the SnO*x* overlayers, the MAPbI3 films did not form a PbI2 diffraction peak, even under strong growth conditions (Figure 5b & Figure S28c, SI and Figure S29c, SI). For the triple-cation perovskites, the residual PbI2 peak did not increase when SnO*x* was grown on top under mild conditions (Figure 5b). However, under strong growth conditions, there was a small increase in the PbI2 peak and small decrease in the intensity of the (002) and (110) perovskite peaks, as well as the appearance of a small peak at 11.7° 2*θ* (Figure S28d, SI and Figure S29d, SI), which we attribute to the appearance of the cesium lead halide delta phase [30]. It has previously been reported that at temperatures above 110 °C, the tetrakis(dimethylamido)tin precursor can remove the FA+ cation from the perovskite [30]. This would agree with our observations, in which the deposition of the SnO*x* overlayer at 150 °C could have removed a small quantity of FA+, resulting in a small increase in PbI2 content and the formation of a cesium lead halide delta phase due to a more Cs-rich perovskite being present. However, we note that the intensity of both the PbI2 and delta-phase peaks remain small, whereas previous reports of ALD or pulsed-CVD SnO2 grown at 150 °C on Cs-FA perovskites resulted in the PbI2 peak being larger than the perovskite (002) & (110) peaks. We attribute the limited bulk damage to the perovskite to the deposition time being significantly shorter (2 min here *vs.* <15 min for pulsed-CVD and ~60 min for ALD) [30]. In addition, our results suggest that MA+ was not as significantly affected by the tin precursor, hence the absence of PbI2 formation in MAPbI3. Overall, our results show the growth of a SnO*x* overlayer to not be as damaging to the bare perovskite films as ZnO, thus showing the importance of looking beyond ZnO for AP-CVD oxide overlayers for lead-halide perovskites.

***2.2.3. Effect of AP-CVD ZnO or SnOx on Perovskite Device Performance***

Consistent with our X-ray diffraction measurements, we found that the growth of a ZnO overlayer led to a significant decrease in device performance, especially for MAPbI3 devices with ZnO grown under strong conditions (Figure 5c&d). This is consistent with an increased PbI2 content in the perovskite films following the deposition of the oxide overlayer. By contrast, the growth of the AP-CVD SnO*x* overlayer under both mild and strong conditions did not lead to an as significant decrease in performance. This is consistent with the X-ray diffraction measurements showing that only a small increase in PbI2 content occurred following the growth of the SnO*x* overlayer on the triple-cation perovskites under strong conditions. Indeed, the growth of SnO*x* using mild conditions led to comparable (MAPbI3) or improved (triple-cation perovskite) performance compared to the control devices (Figure 5c&d).

After optimizing the thickness of the SnO*x* layer (grown under mild conditions) to 60 nm, we achieved a triple-cation perovskite device with a power conversion efficiency of 19.7% (reverse sweep)/19.3% (forward sweep), which was close to the steady-state efficiency of 19.4% (Figure 5e, inset). This was higher than the performance of the control device (16.5% reverse sweep; 16.3% forward sweep; 16.5% steady-state efficiency). The improvement in efficiency was statistically significant, with the SnO*x*-coated devices having an average efficiency of 18±1%, compared to 15±1% for the control. The means were calculated from six devices for each condition, and the average forward and reverse sweep efficiencies were the same. The improvement in performance was primarily due to an increase in the fill factor from 72±2% (control) to 82±2% (60 nm SnO*x*). This correlated with an increase in the shunt resistance from 1300±600  cm2 (control) to 3000±1000  cm2 (60 nm SnO*x*). Our dark current-density *vs*. voltage measurements (Figure 5f) are consistent with a reduction in shunting with the SnO*x* overlayer, in which the coated triple-cation perovskite devices showed lower reverse-bias dark current density and a higher rectification ratio. This is similar to our results with the TiO*x* overlayer and is likely due to the dense oxide covering shunt pathways in the PC61BM layer (Figure S17, SI). We note that we only measured the dark current density curves to -0.2 V because these devices exhibited voltage breakdown at more negative biases. The fill factor of our champion device with AP-CVD SnO*x* was 84%. By contrast, perovskite devices with oxide buffer layers grown by solution-processing and sputter deposition have lower fill factors because of current leakage through less dense films (solution-processing) [64], or because of damage to the perovskite surface and more resistive oxides grown under sub-optimal conditions (sputter deposition) [33]. To our knowledge, the champion steady-state efficiency of 19.4% is currently the highest reported for a perovskite device with an oxide buffer layer deposited by ALD, solution processing or sputter deposition (Table S1, SI).

2.3. Broad Applications of AP-CVD Oxides in Devices

To investigate whether we can apply our AP-CVD SnO*x* to cover textured perovskite films, we grew wrinkled Cs0.17FA0.83Pb(I0.83Br0.17)3 perovskites (Figure 6a). These thin films wrinkle during annealing due to compressive stresses [66], which is achievable by tuning the fraction of dimethyl sulfoxide in the perovskite solvent. After depositing PC61BM by solution processing, clusters and streaks formed (Figure 6b), suggesting non-uniform coverage of the PC61BM. Depositing 20 nm SnO*x* on top resulted in the same morphology as the PC61BM-coated sample, suggesting conformal coverage (Figure 6c). We imaged a cross-section of the sample with PC61BM and SnO*x*, and found that while the PC61BM did not cover some regions of the wrinkled perovskite, the SnO*x* layer was conformal over the entire surface of the sample (Figure S30, SI). The devices with only a PC61BM layer exhibited significant shunting (Figure 6d&e), with fill factors of 38±2% and shunt resistances of only 300±50  cm2. However, after the growth the SnO*x* overlayer, the fill factor increased and reverse-bias dark current density decreased with increasing thickness (Figure 6d&e). Through the use of AP-CVD SnO*x*, we were able to increase the power conversion efficiency from 6.5±0.6% (no oxide; forward sweep) to 10.9±0.5% (115 nm SnO*x*; forward sweep). This has potential future applications in conformally covering evaporated perovskite films grown over textured silicon cells for tandem photovoltaic devices, which are becoming increasingly popular because they have led to the most efficient perovskite-silicon tandems, and industry-standard silicon solar cells are front-textured to reduce light scattering [34,35]. We note that the AP-CVD SnO*x* and TiO*x* films exhibit high transmittances >90% in the visible light wavelength range, rising to >98% in the near-infrared wavelength range (Figure S31a&b, SI). This makes them suitable as buffer layers for a semi-transparent perovskite top-cell that have minimal contribution to parasitic optical losses. We also note that when we grew 60 nm SnO*x* over (Cs,FA)-based perovskites with a more optimized composition and device structure, with less wrinkling, we improved the median efficiency from 14.7% (no SnO*x*) to 15.4% (with SnO*x*; peak value of 16.8%), as detailed in Figure S32, SI.

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**Figure 6.** Atomic force microscopy image of wrinkled Cs0.17FA0.83Pb(I0.83Br0.17)3 thin film (a) with no overlayer, (b) coated with PC61BM and (c) coated with PC61BM and SnO*x*. The color scales in all atomic force microscopy images were adjusted to range from -400 nm to 400 nm. (d) Illuminated current density–voltage curves and (e) dark current density–voltage curves of Cs0.17FA0.83Pb(I0.83Br0.17)3 devices coated with PC61BM and with no oxide (control), 35 nm and 115 nm SnO*x*.

3. Conclusion

Growth of oxide buffer layers over lead-halide perovskites and their organic charge transport layers is critically important for protecting against environmental and mechanical damage, and requires finely-tuned processing parameters compatible with the thermally-unstable perovskite layer. In this work, we have shown AP-CVD to overcome the limitations of the current methods to fulfil all key requirements for growing oxide buffer layers on lead-halide perovskites. AP-CVD films are pinhole-free, can be grown rapidly without vacuum, and are conformal to textured perovskites. The oxides are also uniform over large area (6.25 cm2 in this work), and AP-CVD has the potential to be scaled-up to deposit on the wafer-scale by increasing the width of the gas manifold. Using TiO*x* as the main test material (*x* ~ 2), we found that the short processing times in AP-CVD allowed us to broaden the range of deposition temperatures compatible with the perovskite stack from <110 °C (spin-coating, ALD, sputter-deposition and thermal evaporation) to ≥180 °C (AP-CVD). TiO*x* grown at higher temperature has lower resistivity, resulting in efficiencies improving by >2% in single-junction perovskite solar cells.

More broadly, we showed that AP-CVD can grow uniform SnO*x* (*x* = 1.98±0.07) and ZnO on perovskites, but the ZnO degraded the perovskite, emphasizing the importance of looking beyond ZnO for buffer layers. Using pinhole-free AP-CVD SnO*x* to cover the non-continuous PC61BM layer in triple-cation perovskite devices, we reduced current leakage, resulting in fill factors reaching 84% and steady-state efficiencies increasing from 16.5% (no SnO*x*) to 19.4% (with 60 nm SnO*x*). To our knowledge, 19.4% is currently the highest power conversion efficiency amongst *p*-*i*-*n* structured perovskite solar cells with oxide buffer layers grown by any practical coating method. AP-CVD is therefore a versatile technique that is appealing for manufacturing oxide buffer layers for perovskite optoelectronic devices.

4. Experimental Section

*Growth of oxides by AP-CVD*: The oxide films were grown using the Vertical Cambridge University Close Proximity (V-CUCP) reactor described in our previous work. The metal precursors for TiO*x*, ZnO and SnO*x* were titanium tetrachloride (Fluka, ≥99%), tetrakis(dimethylamido)tin(IV) (Sigma Aldrich; 99.9%), and diethylzinc (Sigma-Aldrich, ≥52%). Both the titanium tetrachloride and diethylzinc were maintained at room temperature, whereas the tetrakis(dimethylamido)tin(IV) was heated to 60 °C. We introduced the metal precursor vapors to the gas manifold by bubbling Ar gas (Air Products, <0.01 ppm O2, <0.02 ppm H2O) through the liquid precursors. We used a flow rate of 25 mL min-1 for the Ti and Zn precursors, but 100 mL min-1 through the Sn precursor. All metal precursor vapors were diluted with Ar gas flowing at 100 mL min-1 (Ti or Zn precursors) or 50 mL min-1 (Sn precursor) before being introduced to the gas manifold. The pipes from the metal precursor to the manifold were maintained at room temperature. For the oxidants, we used O2 gas (Air Products, <1 ppm H2O) or water vapor. The water vapor was produced by bubbling Ar gas through deionized water at room temperature at a flow rate of 100 mL min-1. When we were using O2 as the oxidant, we used a flow rate of 100 mL min-1. The oxidant vapors were diluted with Ar gas flowing at 150 mL min-1 (for growing TiO*x*) or 100 mL min-1 (for growing ZnO) or 200 mL min-1 (for growing SnO*x*). Further we introduced Ar gas flowing at 500 mL min-1 (for growing TiO*x* or ZnO) or 600 mL min-1 (SnO*x*) to the gas manifold. This was then split between four channels that were positioned between the metal precursor and oxidant gas channels. The gas manifold was maintained at 40 °C using circulating water. The substrate was oscillated beneath the manifold at a default speed of 50 mm s-1. This speed was changed if we needed to change the exposure time per cycle to determine the growth regime. We maintained a spacing of 125 µm between the bottom of the gas manifold and top of the substrate using a micrometer for all growths. The temperature of the substrate holder was adjusted to the desired value. A schematic of the V-CUCP setup can be found in Ref. [42].

*Fabrication of perovskite thin films*: To deposit MAPbI3 films, we dissolved CH3NH3I (GreatCell Solar, 90-100%w/w) and PbI2 (TCI, 99.99%) with a 1 mol L-1 concentration in a solution composed of 70 vol.% γ-butyrolactone (Sigma-Aldrich, ≥99%) and 30 vol.% dimethyl sulfoxide (Sigma-Aldrich, ≥99.9%). This solution was mixed at 70 °C for 1 h, before being cooled to room temperature for 30 min and filtered through a 0.45 µm pore PTFE filter (Sigma-Aldrich). The films were grown on 12 mm × 12 mm substrates by spreading 40 µL solution over the substrate and spinning at 1000 rpm for 30 s, followed by 4000 rpm for 60 s. 75 µL toluene (Sigma-Aldrich, 99.8%) was dynamically dripped over the substrate 32 s before the end. The films were annealed at 60 °C for 2 min, followed by 100 °C for 30 min.

To prepare triple-cation perovskite films, we made a solution containing 1 mol L-1 CH(NH2)2I (GreatCell Solar, 90-100%w/w), 0.2 mol L-1 CH3NH3Br (GreatCell Solar, 90-100%w/w), 1.1 mol L-1 PbI2 (TCI, 99.99%) and 0.2 mol L-1 PbBr2 (TCI, ≥98.0%) were dissolved in 51 vol.% *N*,*N*-dimethylformamide (Sigma-Aldrich, 99.8%), 34 vol.% dimethyl sulfoxide (Sigma-Aldrich, ≥99.9%), 15 vol.% 1-methyl-2-pyrrolidone (Sigma-Aldrich, 99.5%). This solution was mixed at 70 °C for 30 min. We also prepared at 1.5 mol L-1 stock solution of CsI (Sigma-Aldrich, 99.999%) in dimethyl sulfoxide, which was also mixed at 70 °C for 30 min. We added 48 µL of the CsI stock solution to 1000 µL of the perovskite solution and mixed at 70 °C for a further 30 min. This solution was then cooled to room temperature for 30 min before being filtered through a 0.45 µm pore PTFE filter (Sigma-Aldrich). The films were grown on 12 mm × 12 mm substrates by spreading 40 µL solution over the substrate and spinning at 1000 rpm for 10 s, followed by 6000 rpm for 20 s. 75 µL chloroform (Sigma-Aldrich, ≥99%) was dynamically dripped over the substrate 5 s before the end. The films were annealed at 100 °C for 30 min. All processing was performed inside a N2-filled glovebox.

The wrinkled Cs0.17FA0.83Pb(I0.83Br0.17)3 perovskites were prepared according to a previously-reported method [66]. 0.17 mol L-1 CsI, 0.83 mol L-1 CH(NH2)2I (GreatCell Solar), 0.75 mol L-1 PbI2 (TCI), 0.26 mol L-1 PsbBr2 (TCI) were dissolved in 80 vol.% *N*,*N*-dimethylformamide (Sigma-Aldrich) and 20 vol.% dimethyl sulfoxide (Sigma-Aldrich) and mixed at 70 °C for 1  h, before being cooled to room temperature for 30 min. The films were grown on 12 mm × 12 mm substrates by spreading 40 µL solution over the substrate and spinning at 1000 rpm for 12 s, followed by 6000 rpm for 30 s. 75 µL chlorobenzene (Sigma-Aldrich, 99.8%) was dynamically dripped over the substrate 11 s before the end. The films were annealed at 50 °C for 1 min, followed by 100 °C for 30 min. All processing was performed inside a N2-filled glovebox.

*Device fabrication*: ITO/glass substrates (Colorado Concept Coatings LLC) were cleaned and had NiO*x* deposited onto them by solution processing. 1 mol L-1 nickel nitrate hexahydrate (Sigma-Aldrich) solution in ethylene glycol (Sigma-Aldrich), complexed with 1 mol L-1 ethylenediamine, was prepared at room temperature and filtered through a 0.45 m PTFE filter (Sigma-Aldrich). This solution was filtered again with a 0.45 m PTFE filter, spread over the ITO-coated glass, and spin-coated at 5000 rpm for 45 s. The films were annealed at 100 °C for 30 min, followed by 300 °C for 1 h in air, then cooled by quenching on a piece of Al foil. The perovskite layers were deposited according to the methods described above. Afterwards, PC61BM (Solenne BV, 99.5%) was deposited on top from a solution of 20 mg mL-1 in chlorobenzene (Sigma-Aldrich) by dynamically dropping 30 µL onto the substrate spinning at 1800 rpm for 40 s, followed by spinning at 3000 rpm for 10 s. For Figure 3, 100 nm Ag was used as the top electrode and deposited by thermal evaporation. A layer of bathocuproine was needed as a layer between the PC61BM and Ag to avoid forming a Schottky barrier. The bathocuproine layer was deposited from a 0.5 mg mL-1 solution in isopropanol (Sigma-Aldrich, anhydrous, 99.5%) by dynamic spin coating at 5000 rpm for 30 s. The other devices in this paper used 100 nm Al directly evaporated onto the PC61BM.

*Characterization*: The film thickness was measured using a Dektak profilometer. A step-edge in the oxide film was created through selective-area deposition, by drawing over a portion of the substrate using marker fluid and removing the marker after the growth of the oxide using acetone. Atomic force microscopy measurements were performed using a Bruker Multimode 8. Silicon tips were used with a cantilever resonant frequency of 319 kHz. Spectroscopic ellipsometry measurements were performed using a J.A. Woolam Co., Inc. EC-400 system using a 75 W Xe light source. Measurements were performed at 60°, 65° and 70°. The wavelength was varied from 245 nm to 900 nm with 1 nm intervals. The Cauchy equation with non-linear optimization code was used to fit the data to obtain values for the thickness, index of refraction and extinction coefficient. For these spectroscopic ellipsometry measurements, the oxides were grown in Si substrates with a 287 nm thick SiO2 layer (as measured spectroscopic ellipsometry). X-ray diffraction was performed using a Bruker D8 theta/theta system. Cu Kα radiation (*λ* = 1.5406 Å) was used as the X-ray source.

Time-resolved photoluminescence measurements were performed by exciting the samples using a 400 nm wavelength frequency-doubled Ti:Sapphire laser (Spectra Physics Solstice). The repetition rate was 1 kHz and pulse length approximately 100 fs. The fluence used was 0.2 mJ cm-2 pulse-1. The photoluminescence spectra were measured at 5 ns time intervals using an intensified charge-coupled device camera with an Andor iStar DH740 CCI-010 system connected to a grating spectrometer (Andor SR303i).

X-ray photoemission spectroscopy measurements were performed using a K-Alpha+ (Thermo Fisher Scientific) spectrometer and another tool equipped with a PHOIBOS 150 (SPECS) electron energy analyzer. Both systems used a monochromatic Al-Kα X-Ray source (*hν* =1486.6 eV). The spectrometer was calibrated according to the standard procedure described in ASTM-E-902-94. High energy resolution peaks were acquired with a 400 µm spot size with a Constant Analyser Energy mode of 20 eV and a 0.1 eV energy step size. No low‐energy electron flood gun for charge compensation was necessary for the analysis. Quantification was performed based on the peak areas after a Shirley type background subtraction using the Thermofisher Scientific Avantage© data system.

Solar simulations were performed using an ABET Technologies Sun 2000 Solar Simulator and Keithley 2623A source-measure unit. Prior to measurements, the solar simulator was calibrated with an NREL certified KG5 filtered silicon reference diode. The scan rate was 100 mV s-1. All devices have an area of 4.5 mm2, but were apertured to 3 mm2 using an Al mask to prevent edge effects. For the resistivity measurements, the oxide was grown on ITO-coated glass. 100 nm Al top electrodes (3.5 mm2 active area) were evaporated over the oxide, and the current – voltage measurements performed inside a glovebox to prevent the oxidation of the Al electrodes in ambient air.

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Author Contributions

R.D.R. and R.A.J. contributed equally to this work. R.L.Z.H. conceived of the project, fabricated the perovskite films and devices, performed the profilometry measurements on the oxide films, and performed the X-ray diffraction and time-resolved photoluminescence measurements. R.D.R. developed the growth of the oxide films by AP-CVD. R.A.J. grew the oxide films and performed the spectroscopic ellipsometry measurements with the help of T.N.H. S.B., W.-W.L., M.B., M.F. and P.S. performed and analyzed the photoemission spectroscopy measurements. T.N.H. performed the atomic force microscopy measurements. M.N. performed the current-voltage measurements for determining the oxide film resistivity. Y.-H.L., M.S. and W.L. contributed to fabricating the perovskite devices and analysis. Z.L. performed the UV-visible spectrophotometry measurements. All authors contributed to writing the paper and discussing the results.

**Declaration of competing interest**

The authors declare no competing interests

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**Appendix A. Supplementary data**

Supporting tables and growth rate, X-ray photoemission spectroscopy, X-ray diffraction, ellipsometry, atomic force microscopy, device, scanning electron microscopy and transmittance measurements available online or from the authors.

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A person wearing glasses and smiling at the camera

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**Ravi Raninga** was a PhD candidate in the Department of Materials Science and Metallurgy, University of Cambridge, working with Prof. Driscoll and Dr. Hoye. His research focus was on developing UV-enhanced atmospheric pressure spatial atomic layer deposition of metal oxides, particularly to achieve low-temperature epitaxy. He completed an integrated Masters degree in Chemistry in 2014 at University College London.

A person smiling for the camera

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**Rob Jagt** **is currently a PhD student at the University of Cambridge, UK, working with Prof. Driscoll and Dr. Hoye. He received his MSc in Econometrics and Applied Physics from the University of Groningen in the Netherlands. After spending a year working with Prof. Julia R. Greer at the California Institute of Technology he moved to the UK to pursue PhD. His main research interests include the development of new energy materials for optoelectronic applications.**

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**Solène Béchu** received her MSc from Clermont University, France in 2012 and completing her PhD in Nantes University, France (2016). After a post-doctoral position at the Institut Photovoltaïque d’Île-de-France, she was appointed associate researcher in 2019 at the Institut Lavoisier de Versailles, CNRS. Her research interests include surface and interface sciences, photoemission spectroscopy techniques, photovoltaics and semi-conductor materials ageing.

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**Tahmida Huq** is currently a PhD student at the University of Cambridge, UK, working with Judith Driscoll and Robert Hoye. She received her MEng degree in Materials Science and Engineering from Imperial College London, UK. After working in industry for 2 years, she returned to academia to complete a MRes in Graphene Technology before starting her PhD. Her primary research interests are in exploring defect tolerant solar absorbers, mainly BiOI, and *n-* and *p-*type metal oxides for use in thin film transistors and charge transport layers in optoelectronic devices.



**Weiwei Li** received his Ph.D degree from Soochow University in 2015. Currently, he is a research associate in the Department of Materials Science & Metallurgy at the University of Cambridge. His research focus on the complex oxide thin films **for (opto-)electronic devices and energy conversion/storage.**

A person wearing a suit and tie smiling at the camera

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**Mark Nikolka** is a Marie-Curie Global Individual Research Fellow at the Cavendish Laboratory and a By-Fellow of Churchill College. He received his PhD from the University of Cambridge in 2016 and spent one year as a research fellow in the Chemical Engineering Department at Stanford University. His research interests include understanding charge transport in conjugated polymers and molecular semiconductors as well as improving the stability of printed semiconductors. More recently, Mark has been working on applying polymer physics to new sensors for the use in stretchable, on-skin biosensors for non-invasive health monitoring.

A person wearing a suit and tie smiling at the camera

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**Yen-Hung Lin** is currently a Postdoctoral Researcher in Prof. Henry Snaith's group in Oxford Physics. After obtaining his BSc and MSc from National Taiwan University, he worked for AU Optronics Corp. (Taiwan) as a senior mobile display engineer. In 2010, he moved to the UK and completed his MSc (2011) and PhD (2015) at Imperial College London with Prof. Thomas Anthopoulos. His research interest lies in the field of large-area energy, electronics and optoelectronics. Currently his research focuses on developing efficient and durable perovskite-on-Si tandem solar cells as well as perovskite optoelectronic neuromorphics.

A person in a red shirt

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**Mengyao Sun** is an undergraduate student at Fudan University, majoring in Materials Chemistry. She worked in Dr. Hoye’s group as an intern in July-September 2019, working on perovskite top-cells for tandem applications. She is currently continuing in this area, working in the Micro Nano System Center at Fudan University.

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**Zewei Li** is a PhD candidate in the Department of Physics at the University of Cambridge, working in the Optoelectronics Group and supervised by Prof. Sir Richard Friend and Dr. Hoye. He is developing lead-free double perovskite thin films for applications in photovoltaics and thin-film transistors. He completed his undergraduate degree in Materials Science at the Harbin Institute of Technology and the University of Manchester. Afterwards, he completed a Masters degree at the University of Cambridge, working with Dr. Robert Hoye.

A close up of a person

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**Wen Li** is currently a Postdoctoral Fellow at the Northwestern Polytechnical University in China and a visiting researcher at the University of Oxford in UK. She received her Ph.D. in Organic Electronics from Nanjing University of Posts and Telecommunications in 2017. Her current research interests focus on the development of nonvolatile organic field-effect transistor memory devices and perovskite-organic hybrid optoelectronic synaptic devices for neuromorphic computing.

A person taking a selfie

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**Muriel Bouttemy** has a PhD in Physico-chemistry. She obtained her doctoral degree in 2006 at Paris XI University (Orsay). After two post-doctoral positions at the Institut Lavoisier de Versailles, she joined the lab as a permanent research engineer on the CEFS2 platform equipped with advanced electron spectroscopies tools. She is partner of the Institut Photovoltaïque d’Île-de-France, and more specifically leader of the chemical characterization task. She is expert in XPS spectroscopy and Scanning Auger Microscopy and her areas of expertise include surface and interface chemistry, surface chemical engineering, multi-scale and multi-techniques methodologies.

**A person wearing a suit and tie smiling and looking at the camera

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**Mathieu Frégnaux** is a Research Engineer at the French National Centre for Scientific Research (CNRS). He completed his PhD at the University of Lorraine (2009–2012), before working as a postdoctoral researcher at the University of Strasbourg (2013–2014) and the French Alternative Energies and Atomic Energy Commission – CEA-LETI (2014-2015). Since 2015, he is managing with Muriel Bouttemy the Center for Study and Training in Electron Spectroscopies (CEFS2) at the Lavoisier Institute of Versailles, equipped with 4 XPS, a SEM-FEG, a GD-OES and an Auger nanoprobe. His research interests include surface and interface science, photoemission, nanomaterials, microelectronics and photovoltaics.

A person wearing a suit and tie smiling at the camera

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**Henry Snaith** is a Professor in the Clarendon Laboratory at the University of Oxford, UK. His work is focused on new materials and device structures for energy and photovoltaic applications. He was one of the early pioneers in the development of high efficiency solid-state organometal halide perovskite-based thin film and meso-superstructured solar cells. In addition, he is a founder of Oxford PV, which is commercializing perovskite-silicon tandem solar cells.

A person smiling for the camera

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**Philip Schulz** is Research Director at the CNRS and pursues his research activities at IPVF, where he leads the Interfaces and Hybrid Materials group installed via a Young Investigator award in the “Make Our Planet Great Again” initiative of the President of the French Republic.   
His interest lies in interface design for organic electronics and hybrid solar cells, which he developed as a postdoctoral researcher at the National Renewable Energy Laboratory (NREL) and at Princeton University, after having obtained his PhD in physics from RWTH Aachen University and including a term abroad at the National Institute of Standards and Technology (NIST) through a DAAD scholarship.



**Judith L. MacManus-Driscoll** is Professor in the Materials Science at the University of Cambridge, Royal Academy of Engineering Chair in Emerging Technologies, and visiting faculty at Los Alamos National Lab. She researches oxide thin film design for low energy electronics and energy materials applications.

A person wearing a suit and tie

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**Robert Hoye** is a Lecturer (Assistant Professor) in the Department of Materials at Imperial College London. There, he also holds a Royal Academy of Engineering Research Fellowship. He completed his PhD at the University of Cambridge (2012–2014), before working as a postdoctoral researcher at the Massachusetts Institute of Technology (2015–2016). He subsequently received two College Research Fellowships at Cambridge, firstly at Magdalene College (2016–2019), then at Downing College (2019–2020), before taking up his Lectureship at Imperial in 2020. His research focusses on defect-tolerant semiconductors, and their development into optoelectronic devices.