Wide-Band-Gap Mixed-Halide 3D Perovskites: Electronic Structure and Halide Segregation Investigation

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ABSTRACT: Mixed-halide organolead perovskites (MAPbX₃) are of great interest for both single-junction and tandem solar cells because of their wide band gap. In this study, we investigate the family of mixed iodide/bromide (I/Br) and bromide/chloride (Br/Cl) perovskites, revealing the strong influence of halide substitution on electronic properties, morphology, film composition, and phase segregation. A qualitative blue shift with the I \rightarrow Br \rightarrow Cl series was observed, with the resulting optical absorption ranging from 420 to 800 nm covering nearly the entire visible region. The ionization potential increases from ≈ 6.0 to ≈ 7.0 eV as the halide composition changes from I to Br. However, with Cl components, the valence band position shows little variation, while the conduction band minimum shifts to a lower value with increasing Cl concentration. By collecting XPS spectra as a function of the sputtering depth, we observed halide segregation in both I/Br and Br/Cl mixed-halide perovskite films, where the large halide ion (I in the I/Br mix or Br in the Br/Cl mix) is preferentially



found on the surface of the film and the smaller halide ion (Br in the I/Br mix or Cl in the Br/Cl mix) accumulates at the bottom of the film. These differences in the band structure, electronic properties, morphology, and film composition impacted the device performance: a decreased short-circuit current density and increased open-circuit voltage were observed with the I \rightarrow Br \rightarrow Cl series. This study highlights the role of halides in the band structure and phase segregation in mixed-halide perovskite solar cells and provides a foundational framework for future optoelectronic applications of these materials.

KEYWORDS: perovskite, electronic structures, photoemission spectroscopy, depth profile, microstructure, phase segregation

INTRODUCTION

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Organic-inorganic hybrid lead-based halide perovskites have been attracting an evergrowing interest, and their certified solar cell power conversion efficiency (PCE) has exceeded 25%. The versatile synthesis of this class of materials offers a wide range of band gaps, and optical and electrical tunability, which makes these materials very attractive for a variety of applications beyond light-harvesting devices, including lightemitting diodes (LEDs),² lasers,³ photodetectors,⁴ photocatalysts,⁵ transistors,⁶ and memory devices.⁷ Wide-band-gap mixed-halide perovskites are promising candidates to boost the PCE of conventional silicon photovoltaics (PV) toward >30% in tandem junction architectures. By stacking complementary wide-band-gap and narrow-band-gap absorbers, the thermalization losses can be largely reduced, and the device can exceed the Shockley-Queisser limit of a conventional single-junction solar cell.^{8,9} For example, in order to match the band gap of a Si cell (\approx 1.1 eV) in tandem devices, a band gap of \approx 1.75 eV for the top cell layer is required.¹⁰

Perovskite-based PVs (with the formula ABX_3) consist of the organic cations (A), including methylammonium (MA⁺), formamidinium (FA⁺), dimethylammonium (DMA⁺), and/or cesium (Cs⁺); and B, which is lead (Pb²⁺) or tin (Sn²⁺); and

halide ions (X), including chloride (Cl), bromide (Br), iodide (I), or the mixture.^{11–18} The PCEs of single-junction perovskite cells have achieved a very high efficiency,^{1,19–23} while the band gaps of these films are around ≈ 1.55 eV, which is too small to match the band gap of Si solar cells in tandem devices. To provide wider-band-gap perovskites, one of the strategies is to develop mixed-halide hybrid perovskites.^{24–27} By integrating wide-band-gap perovskite top cells with silicon bottom cells, PCEs over 28% have been achieved in two-terminal monolithic tandem solar cells.²⁸

However, as the band gaps reach the optimum 1.7-1.8 eV range, fundamental issues, such as photoinstability and photoinduced phase segregation, have been discovered. It has been reported that the increased Br fraction of the X halide ion in MAPb $[I_{(1-x)}Br_x]_3$ under illumination can lead to the formation of light-induced halide segregation and impacts the

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photostability of mixed-halide perovskites. The iodide-rich domains with a smaller band gap increase the subgap absorption, leading to a red shift of the photoluminescence (PL), and reduce the open-circuit voltage (V_{OC}) .^{29,30} Moreover, Chen et al. reported a two-photon confocal microscopy investigation of dynamic photoinduced phase segregation and phase recovery in mixed-halide MAPbBr_xI_{3-x} perovskite single crystals under dark conditions, indicating the Br-phase is dispersed in the interior of the microplatelets while I substitution tends to occur at the crystal edges.³¹ The photoinduced phase segregation can be reduced through the substitution of MA or FA to Cs or DMA while limiting the Br fraction.^{32,33} Phase segregation information can be extracted from the optical or electrical properties using techniques such as absorption and photoluminescence spectroscopy, external quantum efficiency (EQE), transient absorption spectroscopy, and photovoltaic performance.^{28,33,34} However, these techniques characterize the bulk electrical or optical properties of the film and cannot give information about the spatial distribution. In this study, we use X-ray photoemission spectroscopy depth profiling to map the elemental distribution in multihalide perovskites.

In this study, we systematically investigate the role of halide substitution in mixed-halide MAPbX₃ perovskites on their morphology, electronic structures, chemical compositions, and so on, to provide insight into the properties of pure- and mixed-halide MAPbX₃ perovskites in relation to their potential application in photovoltaics. Correlating investigations between the crystal structure, optical properties, and phases are performed for different halide-substituted MAPbX₃ by scanning electron microscopy (SEM), UV-vis absorption spectroscopy, X-ray diffraction (XRD), and ultraviolet and Xray photoemission spectroscopy (UPS and XPS). The formation of pinhole-free high-quality mixed-halide perovskite films was confirmed by SEM and XRD studies. The band structure can be effectively tuned by precise control over the halide composition in MAPbX₃ films. Halide inhomogeneity was observed in mixed-halide perovskite films, as evidenced by the XPS depth profile. This fundamental information about the MAPbX₃ perovskite films can be expected to guide the synthesis of new perovskite films and the design of optimal cell structures.

RESULTS AND DISCUSSION

To study the effects of halide substitution on the properties of MAPbX₃ perovskite films, precursor solutions with desired reaction ratios were prepared and then spin-coated on the substrate using the one-step deposition protocol with chlorobenzene (CB) as antisolvent, followed by thermal annealing treatment (see Experimental Details). The resulting films include MAPbI₃, MAPbI_{1.5}Br_{1.5}, MAPbBr₃, MAPbBr_{1.5}Cl_{1.5}, and MAPbCl₃. The morphology of the hybrid perovskite thin films can be controlled through the solvent engineering approach via a dripping antisolvent. This method has been widely used in the one-step classic MAPbI₃ deposition. The antisolvent dripping at an optimized timing during spin coating of the perovskite ink is critical for uniform films.^{35,36}

Morphology and Crystal Structures. First, we investigate the morphology using scanning electron microscopy (SEM) from small-band-gap MAPbI₃ to wider-band-gap hybrid halide perovskites by mixing Br and Cl halides. Appropriate use of CB dripping has been shown to enable

quick extraction of the precursor dimethyl sulfoxide (DMSO) solvent and increase nucleation and crystal growth to reveal a high-quality and fully covered perovskite morphology on substrates with fewer pinholes.^{36,37} Figure 1a–e shows the



Figure 1. Surface morphologies and XRD spectra of tunable-band-gap perovskite thin films: (a, f) MAPbI₃, (b, g) MAPbI_{1.5}Br_{1.5}, (c, h) MAPbBr₃, (d, i) MAPbBr_{1.5}Cl_{1.5}, and (e, j) MAPbCl₃ films on ITO substrates. The scale bar is 1 μ m.

representative SEM images of pure- and mixed-halide MAPbX₃ perovskite films. The SEM images show that all five films have good surface coverage and film uniformity on the substrates with different grain sizes and irregular grain boundaries. The various grain sizes of these perovskite films may be attributed to the different nucleation and crystallization processes, by which the wide-band-gap MAPbBr3 and MAPbCl3 perovskite phase forms directly from the disordered solvate phase during solution processing, whereas MAPbI₃ ink tends to form intermediate ordered sol-gel phases requiring further thermal annealing to form the $MAPbI_3$ perovskite phase.^{35,38,39} As shown in Figure 1d,e, the incorporation of chlorine leads to the formation of a few pinholes. The origin of these pinholes is likely due to the nucleation and growth behavior of intermediate phases other than the perovskite phase, which can have different unit cell sizes that lead to cracking upon transformation into the perovskite phase.

To understand the impact of halide modification on the microstructure of the polycrystalline hybrid perovskite layers, XRD was performed on these films. Figure 1f shows the XRD patterns of the tetragonal-phase MAPbI₃ perovskite films. The peaks at 14.1, 28.4, and 31.7° were attributed to the (110), (220), and (310) diffraction planes of the MAPbI₃ perovskite polycrystalline structures, respectively. Notably, there is only a (110) diffraction peak at 14.1° from the MAPbI₃ perovskite phase without the non-perovskite PbI₂ diffraction peak featured at 12.6°, indicating complete MAPbI₃ perovskite determine the films is also verified via ex situ XRD

measurements. The peak of the (100) diffraction plane shifts from 14.5 (MAPbI_{1.5}Br_{1.5}, Figure 1g), 15.1 (MAPbBr₃, Figure 1h), 15.4 (MAPbBr_{1.5}Cl_{1.5}, Figure 1i), to 15.7 (MAPbCl₃, Figure 1j) degrees, indicating a decrease in lattice spacing in these cubic perovskites, which is caused by the decreasing size of the halide ions.^{40,41} The structural changes of the unit cells from tetragonal (MAPbI₃) to cubic (other pure- and mixedhalide perovskite films) alter the lattice constant. It has been reported that the cubic phase is usually more stable than the tetragonal phase.^{42,43} To conclude, the polycrystalline structure of perovskite thin films can be effectively altered through the simple one-step spin coating of precursor solutions with different halide ratios.

Band Structure and Energetics. To map out the band structure as a function of halide content, we investigate the energetics of the occupied states and band gaps using ultraviolet photoemission spectroscopy (UPS) and UV–vis absorption spectroscopy, respectively. UV-Vis absorption spectra and photographs of the perovskite films were obtained and are shown in Figure 2a. As shown in the inset, the film



Figure 2. (a) UV-vis absorption spectra of mixed-halide perovskite films. Inset: photographs of each perovskite thin film. (b) Schematics of the electronic structure of the mixed-halide perovskite films near the band-gap region. (c) UPS secondary electron edge (SEE) and the low-binding energy region (near the Fermi energy $E_F = 0$ eV) of mixed-halide perovskite films. The onset of ionization of filled states relative to zero binding energy is used to track the shifts of E_F relative to VBM.

color changes from dark black to orange, then to semitransparent yellow, and becomes transparent with increasing the Br or Cl content in the perovskite structure. The gradual shifts in the absorption edge from 1.6 to 3.1 eV are observed as I is replaced by Br and then by Cl, with the optical band gaps being calculated from the Tauc plot (Figure S3, Supporting Information). This is caused by the decreased length of the Pb–X bonds within the network of the corner-sharing octahedra as the ion size changes (Pb– X_{6} , X = I, Br, Cl).^{44,45} An increased excitonic pre-peak related to the increasing exciton binding energy was also observed as the halide changed from I to Br and Cl. These observations are consistent with the previously reported literature.⁴⁴ As the band gap increases, the hybrid perovskite thin films can absorb light from high-energy visible to ultraviolet sunlight radiation and convert to electricity.

Figure 2c shows the high-binding-energy cutoff region (i.e., secondary electron edge, SEE) and the low-binding-energy part of the UPS spectra as a function of the halide substitution, in which all energies are referenced to a common Fermi Level $(E_{\rm f} = 0 \text{ eV})$. The work function ϕ was determined from the high-binding-energy cutoff region (i.e., secondary electron edge, SEE), given by the difference between the energy of the UV photons (21.21 eV for the He I radiation used here) and the binding energy of the SEE $(E_{\rm f} = E_{\rm He(I)} - E_{\rm SEE})$. The ionization energy (IE) can be extracted from the energy difference of the valence band maximum (VBM) relative to the vacuum level (E_{VAC}) . The detailed evolution of UPS spectra and the standard deviation from averaging the results obtained with different samples and spots are summarized in the Supporting Information (Table S1). The corresponding energy diagrams of the perovskite films are summarized in Figure 2b. It is noted that the Fermi level is close to the conduction band minimum (CBM), indicating that all of these perovskite films function as n-type semiconductors. Both n- and p-type transports have been reported for perovskite field-effect transistors.⁴⁶⁻⁴⁸ Self-doping effects have been observed in perovskite films where the charge transport type can be controlled by changing the precursor ratios and post-treatment condition.^{49,50} In our work, all of the films were prepared with 1:1 methylammonium halide (MAX) to lead halide (Pb X_2) precursor ratios and annealed at 100 °C for 10 min, both of which will lead to the n-type behavior of perovskite films. The position of the CBM (E_{CBM}) is calculated from the position of VBM and the band-gap value. MAPbI $_3$ yielded the smallest ϕ of 4.58 eV and IE of 6.01 eV. Full substitution of I to Br and Cl increase the ϕ to 5.14 and 4.86 eV, and IE to 6.99 and 6.95 eV, for MAPbBr3 and MAPbCl3 films, respectively. For the mixedhalide films, MAPbI₁₅Br₁₅ and MAPbBr₁₅Cl₁₅, the position of ϕ and IE lie in between the pure-halide films. It is worth noting that the IE increases from ≈ 6.0 to ≈ 7.0 eV as the I is substituted by Br, while little variation is observed when Br is substituted by Cl and a monotonic trend is found for the conduction band edge. These numbers are slightly different from the literature reported value,^{44,51} which may be attributed to variations in grain structure and morphology caused by different film processing and post-treatment conditions. Different grain structures and morphologies will lead to different perovskite phases, band structures, and halide compositions; thus, it would be difficult to make a direct comparison between films reported in different literature studies. The UPS is mostly sensitive to the top 2-3 nm surface region due to the lower kinetic energy of the emitted photoelectrons (21.2 eV), and surface contaminants may impact the measured UPS spectra during the film preparation and transfer.

Composition Analysis. Figure 3 shows the evolution of XPS C 1s, N 1s, Pb 4f, I 3d, Br 3d, and Cl 2p spectral regions in the mixed-halide perovskite films. The elements are fitted by using Lorentzian–Gaussian peaks. The C 1s core-level spectra



Figure 3. Representative XPS core-level spectra of (a) C 1s, (b) N 1s, (c) Pb 4f, and (d) I 3d in MAPbI₃, (e) Br 3d in MAPbBr₃, and (f) Cl 2p in MAPbCl₃ perovskite films.

from all of the films contain two components: one at \approx 284.5 eV, which is assigned to surface-absorbed amorphous carbon, and another at \approx 285.9 eV, attributed to the C-N bond in MA⁺ and FA⁺ cations, according to the literature.^{52,53} The presence of MA cations is also confirmed by the N 1s peak at 401.9 eV. The Pb 4f spectra from the MAPbI₃ film show a sharp doublet located at 138.0 eV (Pb $4f_{7/2}$) and 142.9 eV (Pb $4f_{5/2}$), which are assigned to the Pb²⁺ metal ion. The peak positions of I 3d_{5/2}, Br 3d_{5/2}, and Cl 2p located at 618.8, 67.8, and 196.2 eV, respectively, are also consistent with the literature reports.⁵² Except for the C 1s, all of the other elements' core levels consist of only one oxidation state, indicating homogeneous films with these elements existing as only one chemical species within the perovskite films. The XPS core-level spectra of these elements in mixed-halide perovskite films are summarized in Figure S2.

To further analyze the distribution of components throughout the film, we measured the depth profile of the five perovskite films by XPS in the dark within a high-vacuum chamber. During the measurement, a 1 keV Ar ion gun was used to etch the sample and spectra were acquired layer by layer until the observation of an abrupt decrease in the Pb 4f signal with an increase in the O 1s and Sn 3d signals from the substrate. The sputtering rate used here was controlled to ≈ 0.2 nm s⁻¹ to minimize sputtering-induced physical damage and the sputtering time was converted to depth assuming a constant etch rate (refer to Experimental Details). It has been reported that sputtering beam-induced artifacts within perovskites can be reasonably neglected when using fast analysis conditions during which the exposure time is limited to a few hours.⁵⁴ The film thicknesses were measured by profilometry and ellipsometry and are reported in the Supporting Information (Figure S1 and Table S2). Figure 4 illustrates the perovskite film elemental composition as a function of the



Figure 4. Representative XPS depth profiles of (a) MAPbI_{1.5}Br_{1.5} and (c) MAPbBr_{1.5}Cl_{1.5} perovskite films. The atomic ratios of halides and metal cations relative to lead Pb²⁺ in (b) MAPbI_{1.5}Br_{1.5} and (d) MAPbBr_{1.5}Cl_{1.5}. Error bars indicate the standard deviation obtained by averaging the results from different spots.

depth determined by XPS using in situ Ar⁺ sputtering. The depth profiles of MAPbI15Br15 and MAPbBr15Cl15 are shown as an example. The surface-absorbed amorphous carbon is evident on the top surface, and no other surface contamination is observed. The C 1s and O 1s fractions are reduced mainly after the first sputter cycle, and the Pb 4f and I 3d fractions from the perovskite layer increase, indicating the removal of the surface-absorbed carbon and oxygen. To better present the film composition, the atomic ratios of halides (I 3d and Br 3d) to lead Pb²⁺ (Pb 4f) in MAPbI_{1.5}Br_{1.5} and MAPbBr_{1.5}Cl_{1.5} films are summarized in Figure 4b,d. The I/Pb ratios in MAPbI_{1.5}Br_{1.5} films decrease from \approx 1.96 to \approx 1.74, accompanied by increasing Br/Pb ratios from ≈ 0.51 to ≈ 1.08 as the depth increases, suggesting a bromide-poor phase was formed close to the film surface and a bromide-rich phase was present close to the substrate. This halide segregation was also observed in the MAPbBr1.5Cl1.5 film, in which the decrease of Br/Pb ratios from \approx 1.90 to \approx 1.63 was accompanied by increase in the Cl/Pb ratios from ≈ 0.75 at the surface to ≈ 1.26 as the depth increased. By tracing the variation of the X/Pb ratios in mixed-halide perovskites, we found that the heavier halide ions tend to accumulate on the surface while smaller halide ions aggregate at the bottom of the film. Similar results were observed in the literature for I and Br mixed-halide perovskite films.^{55,56} It has been reported that an intrinsic perovskite favors electron trapping at the top surface, which induces an electric field pointing toward the surface of the film.^{57–59} To shield the trap-induced field and compensate the charge on the surface, the mobile halide ions tend to migrate away from the surface and leave the positively charged vacancies accumulated near the surface states.⁶⁰ In the mixed-halide films, smaller ions (such as bromide in MAPbI_{1.5}Br_{1.5}, or chloride in MAPbBr_{1.5}Cl_{1.5}) are relatively easy to migrate, thus leaving the heavier ions to accumulate on the surface. The DFT calculation also shows that the segregation of smaller ions to the surface is energetically disfavored, while accumulation of heavier ions toward the surface leads to an overall stabilization.⁶¹

The device performance of each wide-band-gap perovskite was investigated using solar cells. Representative J-V curves are shown in Figure 5b. For classic and low-band-gap MAPbI₃



Figure 5. (a) Schematic diagram of the solar cell devices. (b) J-V curve for the peak efficiency of mixed-halide perovskite solar cells under AM1.5G illumination.

solar cells, the average $16.25 \pm 0.92\%$ of PCE is demonstrated, prepared with the same spin-coating recipe. A summary of the photovoltaic parameters (Table 1) obtained from all of the perovskite solar cells contains both average and best values. While changing the halide from I to Br, and then to Cl in these wide-band-gap perovskites, the average PCE ranges from 16.25

to 10.87, 6.51, 1.08, and to 0.29%, and short-circuit current density (I_{SC}) decreases due to the enhancing band gap in MAPbI₃, MAPbI_{1.5}Br_{1.5}, MAPbBr₃, MAPbBr_{1.5}Cl_{1.5}, and MAPbCl₃ films. The decreased J_{SC} is due to the increasing band gap leading to less sunlight absorption. The high average fill factor is stable around 68-77% across all of the films. A high V_{OC} is maintained around 1.4 V for MAPbBr₃ and MAPbBr_{1.5}Cl_{1.5} solar cells, even though MAPbBr_{1.5}Cl_{1.5} has a wider band gap and an ultrahigh $V_{\rm OC}$ of 1.65 V is achieved in MAPbCl₃ perovskite devices. The pinned V_{OC} may be attributed to the activation energy for these wide-band-gap solar cells that is much lower than the band gap. This suggests that a high interface recombination process limits the $V_{\rm OC}$ and, consequently, the device performance of these wide-band-gap solar cells.⁶² To overcome this problem, an investigation of alternative electron or hole transporting layers or surface modification is needed in the future.⁶² It is worth noting that the best perovskite device performance for $MAPbCl_3$ is PCE = 0.32% with $V_{\rm OC}$ = 1.65 V. This MAPbCl₃ transparent perovskite thin film with an extremely high-V_{OC} perovskite solar cell is also very promising in the applications of building integrated photovoltaic systems, blue and ultraviolet lightemitting diodes, and photodetectors.

CONCLUSIONS

In summary, we systemically investigate the electronic properties, morphology, film composition, and phase segregation of a series of mixed-halide MAPbX₃ (X = Cl, Br, and I) perovskite films. Pinhole-free, high-quality MAPbX₃ hybrid perovskite thin films were fabricated by a simple one-step spincoating method with antisolvent dripping. Structural measurements show that I can be seamlessly substituted by Br and then by Cl, attributed to the lattice compatibility of the pure-halide composition. A full tunability of ionization potentials was observed along with the I \rightarrow Br \rightarrow Cl series, and the light absorption of the resulting films covers the entire visible region. We also unravel the roles of the halide in promoting vertical homogeneous composition distribution in perovskite films, thus preventing segregation of halides and cations. Moreover, halide inhomogeneity was observed in mixed-halide perovskite films by using XPS depth profiling. In mixed-halide perovskite films (MAPbI_{1.5}Br_{1.5} and MAPbBr_{1.5}Cl_{1.5}), smaller halide ions tend to aggregate at the bottom of the perovskite films, leaving a higher concentration of larger halide ions on the surface. Although only two systems were studied, it provides insight into how halide ions might be distributed in mixed-halide perovskite films. This study provides an in-depth understanding of tunable- and wide-band-gap perovskite inks, which is critical and insightful for the initial design of perovskite precursor solutions to achieve better reproducibility and for cost-efficient and large-scale manufacturing of leadbased hybrid perovskite solar cells in the future.

EXPERIMENTAL DETAILS

Materials and Film Preparation. All the commercial materials and instruments mentioned here are for the purpose of fostering understanding. These identifications do not imply recommendation by the NIST. It also does not imply that the materials or equipment identified are necessarily ones with the best performance. All of the chemicals were purchased from Sigma–Aldrich unless stated otherwise. Cl-TiO₂ was synthesized according to the published recipe.¹¹ The Cl-TiO₂ nanocrystal solutions were spin-coated on a glass substrate followed by annealing at 150 °C for 30 min in ambient

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perovskites		$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA~cm^{-2}})$	FF (%)	PCE (%)
MAPbI ₃	average	1.04 ± 0.03	21.88 ± 0.53	71.19 ± 2.51	16.25 ± 0.92
	best	1.09	22.19	71.65	17.33
MAPbI _{1.5} Br _{1.5}	average	1.15 ± 0.02	13.85 ± 0.60	68.30 ± 0.86	10.87 ± 0.69
	best	1.19	14.60	69.40	12.06
MAPbBr ₃	average	1.38 ± 0.03	6.13 ± 0.15	76.97 ± 1.50	6.51 ± 0.26
	best	1.40	6.31	78.30	6.92
MAPbBr _{1.5} Cl _{1.5}	average	1.40 ± 0.01	1.13 ± 0.12	68.21 ± 4.91	1.08 ± 0.13
	best	1.41	1.26	69.04	1.23
MAPbCl ₃	average	1.64 ± 0.03	0.26 ± 0.03	67.82 ± 2.66	0.29 ± 0.03
	best	1.65	0.28	69.44	0.32

Table 1. PV Parameters of Classic MAPbI₃ and Wide-Band-Gap MAPbI_{3-x}Br_x and MAPbBr_{3-x}Cl_x (x = 0-3) Hybrid Perovskite Solar Cells

air. The thickness of Cl-TiO₂ is about 50 nm. For solar cell devices, prepatterned ITO (ITO: 15 Ω sq⁻¹—bought from Xinyan Technologies) glass substrates were used. The perovskite precursor (1M) solution was prepared by dissolving methylammonium halide (MAI, MABr, MACl), purchased from Dyesol, and each lead halide (PbI₂, PbBr₂, PbCl₂) (1:1 ratio) in dimethyl sulfoxide (DMSO) and stirring overnight at 60 °C. Thin films of perovskites were deposited by spin coating at 1000 rpm for 10 s and 5000 rpm for 50 s. Chlorobenzene (0.25 mL) was dropped on the spinning substrate during the second spin-coating step at 30 s before the end of the spinning. The films were then annealed at 100 °C for 10 min.

Solar Cell Fabrication. Perovskite was prepared as above, and after cooling to room temperature, the hole-transporting layer was deposited on the perovskite film via spin-coating at 2000 rpm for 30 s using chlorobenzene of a 80 mg mL⁻¹ solution of 2,2',7,7'-tetrakis-(N,N-di-methoxyphenamine) 9,9'-spirobifluorene (spiro-MeOTAD), with additives of lithium bis(trifluoromethanesulfonyl) imide and 4-*tert*-butylpyridine. Finally, 20 nm of gold (Au) and 80 nm of silver (Ag) electrodes were deposited by thermal evaporation using an Angstrom thermal evaporator. The current-density–voltage (J-V) curves were measured using a solar simulator (Newport, Oriel Class A, 91195A) with a source meter (Keithley 2420) at 100 mA cm⁻² illumination (AM 1.5G) and a calibrated Si-reference cell certificated by NREL. All of the solar cells were masked during the J-V measurements to define the active area of about 0.1 cm².

Characterization. *Scanning Electron Microscopy (SEM).* A Quanta 200FEG scanning electron microscope from FEI was used to observe the morphology of the annealed perovskite films.

UV-Vis Transmission Measurements. UV-vis absorption spectra were acquired using a Cary 5000.

X-ray Powder Diffraction. XRD patterns were obtained using a Bruker D8 advance A25 diffractometer in the Bragg–Brentano geometry equipped with a Cu tube (Cu K α ; λ = 0.15418 nm) operating at 40 kV and 40 mA with a linear-position sensitive detector (opening at 2.9°).

Photoemission Spectroscopy Measurements. Ultraviolet photoemission spectroscopy (UPS) and X-ray photoemission spectroscopy (XPS) spectra were acquired using the Kratos Axis Ultra^{DLD} analysis system. UPS was conducted using a He-I lamp radiation (21.2 eV), while XPS was done using the monochromatic Al K α line.⁶³ The films were kept inside the analysis chamber with a base pressure of $<10^{-6}$ Pa during the measurements. All samples were characterized at a normal takeoff angle. A copper tape was put in contact with the perovskite film to reach electronic equilibrium. The UPS spectra were acquired under 5 eV pass. The Fermi level was calibrated using a sputter-cleaned Au sample. The high-resolution XPS spectra were collected with 20 eV pass energy. Ar ion sputtering was performed with a power of 1 keV and 600 nA. The XPS spectra were collected after 150 s of sputtering time. It took about 1500 s to fully etch through a 400 nm film; thus, the sputtering rate is estimated to be 0.27 nm s⁻¹. The film thickness was measured by using ellipsometry and a profilometer. All of the results are shown in the Supporting Information (Figure S2).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaelm.1c00191.

Summary of the band structure and energy levels (Table S1); profilometry; ellipsometry (Figure S1 and Table S2); XPS spectra (Figure S2); and Tauc plot of perovskite films (Figure S3) (PDF)

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Author Contributions

S.Z. and M.-C.T. contributed equally to this work. S.Z., M.-C.T., T.D.A., and C.A.H. conceived and planned the experiments. S.Z. performed the UPS and XPS measurements. M.-C.T. prepared the samples and performed the UV–vis and

SEM measurements, and performed solar cell fabrication and characterization. N.V.N. measured and simulated the ellipsometry spectra. All authors provided critical feedbacks and helped to shape the research, analysis, and manuscript.

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Notes

The authors declare no competing financial interest.

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