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ABSTRACT
Mixed-halide perovskites enable bandgap engineering for tandem solar cell and light-emitting diode applications. However, photoinduced halide phase segregation introduces a compositional instability, that is, formation of I-rich and Br-rich phases, which compromises photovoltaic efficiency and stability. While optical and structural studies of the photoinduced phase segregation in mixed-halide perovskites have been reported, its impact on the material stability is missing. Here, a detailed compositional analysis of mixed-halide perovskite films using x-ray and ultraviolet photoelectron spectroscopy (UPS) was carried out to determine how their stability in various environments depends on the halide ratio. A series of perovskite thin films were fabricated with the composition CH$_3$NH$_3$Pb(I$_x$Br$_{1-x}$)$_3$, where x = 0.00, 0.25, 0.50, 0.75, and 1.00, and analyzed under different conditions, such as exposure to light in ambient and in nitrogen atmosphere, as well as storage in the dark. From the spectroscopy results, complemented with structural and optical properties, it was found that the deletion of halide ions from the surface is facilitated in mixed-halide perovskites in comparison with pure halide perovskites. A higher stability was found for the mixed-halide perovskite containing less than 25% Br, and it decreases with increasing Br content. This study also established the effect of the Br/I ratio on the energy landscape of the materials. The UPS spectra reveal that photoinduced degradation results in a mismatch of the energy levels at the perovskite/transport layer interface, which may limit the collection of charge carriers. These findings correlate well with the photovoltaic device stability under similar degradation conditions.

I. INTRODUCTION
Organic–inorganic hybrid halide perovskites (OIHPs) gained huge attention in the photovoltaic (PV) community due to their skyrocketing efficiency in a short span of time. Lead halide perovskites have exceptional opto-electronic properties, such as high defect tolerance, long carrier diffusion length, sharp absorption edge, ambipolar nature, and long carrier recombination lifetime. The efficiency of perovskite solar cells (PSCs) exceeds 25% for single-junction and 30% for perovskite–Si tandem solar cells. The ideal bandgap for the top cell of a perovskite–Si tandem solar cell is predicted to be ~1.73 eV. However, most of the highly efficient single-junction PSCs have a bandgap of ~1.6 eV. Mixed-halide perovskites offer a route to achieve tunable wider bandgaps for tandem solar cells and are promising materials for light emitting diode applications. However, the iodine–bromine mixed-halide perovskite suffers from phase segregation into I-rich and Br-rich regions under visible light illumination. Hoke et al. showed that the phase segregation in mixed I–Br perovskites leads to the formation of smaller bandgap trap states, which is responsible for decreased efficiency. The photoinduced phase segregation is well established in mixed-halide perovskite solid thin films and single crystals and has been studied by various optical techniques, such as photoluminescence (PL), absorption, two-photon PL microscopy, and transient absorption. The thermodynamic origin of phase segregation in perovskite is explored by density functional theory (DFT) and molecular dynamics simulations. The findings show that upon illumination, the...
charge carrier induced lattice distortion results in an increase in the free energy of mixing with composition, which drives the segregation into small bandgap (I-rich) and wide bandgap (Br-rich) regions. It is also reported that the nature of the A-cation and presence of contact layers can play a significant role in the phase segregation. Jaffe et al. showed that external pressure can mitigate the phase segregation in perovskites. However, commercial solar cells cannot be operated under external high pressure. It is found that mixed organic-cation perovskites show enhanced phase stability due to the effect of chemical pressure. Lim et al. demonstrated that top coating a mixed-halide perovskite film with a hole transport layer (HTL) leads to suppression of phase segregation. It is found that the I-rich region formed at the perovskite/HTL interface enhances the back transfer of holes from the HTL through improved energy level offset. Zhao et al. studied the effect of grain boundaries on the light-induced halide segregation in mixed halide perovskite films through scanning probe PL microscopy. It is reported that the PL peak position remains stable for a mixed-halide perovskite film with low Br (35%) concentration when the laser was focused on the grain centers. However, PL emission from grain boundaries shows evident light-induced halide segregation. For a mixed-halide perovskite film with a high Br (65%) concentration, both the grain centers and grain boundaries show PL splitting, which suggests that halide segregation occurs in the whole perovskite layer. Hoke et al. found that the mixed-halide perovskite can be cycled between segregated and unsegregated (single phase) states repeatedly without any degradation in the material. Despite the progress in the phase stability of mixed-halide perovskites, their practical implementation requires an understanding of the effect of phase segregation on their stability under operational conditions, in particular their photochemical stability, when exposed to ambient air and light. Examining the changes in chemical composition and electronic structure of the mixed-halide perovskites under humidity and solar illumination conditions will yield a better understanding of their photochemical stability. There are several reports on the photochemical degradation of pure halide perovskites from the chemical point of view, but to the best of our knowledge, very few reports on the photochemical degradation of the mixed-halide perovskites. Sekimoto et al. investigated the influence of the HTL on light-induced compositional changes of mixed OIHHP solar cells through hard x-ray photoelectron spectroscopy (HAXPES) and their electronic properties through impedance spectroscopy. However, this study is limited to a single perovskite composition, and the impact of halide concentration on the material/device stability and electronic structure of the perovskite absorber is not addressed.

In this study, we fabricated a series of lead-based mixed-halide perovskite films with composition CH$_3$NH$_3$Pb$_x$I$_{3-x}$Br$_x$, where x = 0.00, 0.25, 0.50, 0.75, and 1.00 on indium tin oxide (ITO) coated glass substrates. X-ray photoelectron spectroscopy (XPS) is used to examine the photochemical degradation in these films using a complete set of XPS measurements, including survey scans, core level spectra, and valence band spectra. In this study, we expose the samples to three different environments to distinguish three types of degradation: (a) chemical degradation (CH) of samples that were kept in the dark in an ambient atmosphere for 1 h with relative humidity (~50 ± 5%) and temperature ~23°C, (b) photo-degradation (PH) of samples that were kept in nitrogen atmosphere and illuminated under 1 Sun (100 mW/cm$^2$) for 1 h, and (c) photochemical degradation (PHCH) of samples that were kept in ambient atmosphere and illuminated under 1 Sun for 1 h. This study reveals the consequences of phase segregation on the material stability of mixed-halide perovskite thin films under different degradation conditions, as compared with pure halide-based perovskites (CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$). Furthermore, ultraviolet photoelectron spectroscopy (UPS) was utilized to understand the changes in energetic landscape of mixed halide perovskite films under similar degradation conditions and to correlate those with the device stability.

II. EXPERIMENTAL SECTION

A. Materials

Lead acetate trihydrate [Pb(Ac)$_2$-3H$_2$O], poly[bis(4-phenyl) (2,4,6-trimethylphenyl)amine] (PTAA), poly(9,9-bis(3′-(N,N-dimethyl)-N-ethy lammonium-propyl)-2,7-fluorene-alt-2,7-(9,9-dioct yfluorene)] dibromide (PFN-Br), hypophosphorous acid (HPA), and bathocuproine (BCP) were purchased from Sigma-Aldrich. Methylammonium iodide (MAI) and methylammonium bromide (MABr) were purchased from TCI chemicals. [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM, 99%) was purchased from Solenne BV. All solvents [dimethylformamide (DMF), toluene, chlorobenzene, 2-propanol, and methanol] were purchased from Sigma-Aldrich. All the materials were used as received.

B. Solution preparation

40 wt. % CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ perovskite precursor solutions were prepared using Pb(Ac)$_2$-3H$_2$O and MAI or MABr in the molar ratio of 1:3 in dimethylformamide (DMF), respectively. 3 µl HPA was added in 1 ml of both the pure halide perovskite precursor solutions, separately, and stirred at room temperature for 4 h. The two pure halide-based perovskite solutions were mixed in the volumetric ratio of x = 0.00, 0.25, 0.50, 0.75, and 1.00 to form CH$_3$NH$_3$Pb$_x$I$_{3-x}$Br$_x$ perovskite precursor solutions. The mixed-halide-based perovskite solutions were stirred for another 2 h at room temperature before use. 1.5 mg of PTAA was dissolved in 1 ml of toluene and kept for overnight stirring at room temperature. 0.5 mg of PFN-Br was dissolved in 1 ml of methanol and kept for overnight stirring at room temperature. 20 mg PC$_{61}$BM was dissolved in 1 ml of chlorobenzene and kept for overnight stirring at room temperature. 0.5 mg BCP was dissolved in 1 ml of 2-propanol and kept for overnight stirring at room temperature. The BCP solution was kept at 70°C for 15 min before use.

C. Perovskite film and device fabrication

The perovskite thin films were fabricated on indium doped tin oxide (ITO) coated glass substrates (purchased from Kintec Company Hong Kong with a sheet resistance of 10 Ω/sq). The substrates were cleaned sequentially with soap solution, deionized water, acetone, and isopropanol for 10 min in an ultrasonic bath. The clean substrates were transferred to the ultraviolet (UV) ozone chamber to enhance the wettability of the substrates and to remove surface contamination. After UV ozone treatment for 20 min, the substrates were transferred to a nitrogen-filled glovebox.
with maintained H₂O and O₂ levels (<0.1 ppm). The PTAA solution was spin-coated at 2000 rpm for 30 s with an acceleration of 500 rpm/s and annealed at 100 °C for 10 min. The substrates were let to cool down on the workbench in the glovebox for 5 min. After that, the PFN-Br solution was spin-coated on top of the PTAA-coated ITO substrate at 5000 rpm for 30 s with an acceleration of 1000 rpm/s. The pure and mixed halide perovskite precursor solutions were spin-coated on the prepared PFN-Br/PTAA/ITO substrate at 4000 rpm for 30 s with an acceleration of 1000 rpm/s. The spin-coated perovskite films were dried at room temperature for 5 min on the workbench and then annealed at 100 °C on a hotplate for 5 min. The PCBM solution was spin-coated onto the perovskite layer at 2000 rpm for 30 s and kept for bench dry for 5 min inside the nitrogen-filled glovebox. After that, the BCP solution was spin-coated over the PCBM/perovskite layer at 5000 rpm for 20 s and no annealing is required in this process. Finally, the devices were transferred to a vacuum chamber (1 × 10⁻⁶ mbar) for silver (Ag) electrode evaporation of thickness 80 nm. The device area was defined as 4.0 mm² by a metal shadow mask.

D. Characterization

The XPS measurements were performed in a ultra-high vacuum (UHV) system equipped with Scienta-Omicron SES-100 electron analyzer and a non-monochromatic x-ray source (Al-Kα = 1487 eV). The base pressure of the UHV system prior to XPS measurements was about 2.0 × 10⁻¹⁰ mbar. During measurements, the pressure in the XPS chamber was 4.5 × 10⁻¹⁰ mbar. Pass energies of 20 and 100 eV were used for core level and survey spectra, respectively. A pass energy of 20 eV was also used for valence band spectra. The electron analyzer was calibrated by measuring the Fermi level (E_F = 0) and Au 4f7/2, peak maximum at 840.0 eV on a clean Au surface. The x-ray gun was operated at 150 W. The freshly prepared samples and samples degraded in nitrogen were transferred from the nitrogen atmosphere of the glovebox to the UHV system without contact with air, using a UHV compatible transfer system. XPS data processing was first performed using the CasaXPS 2.3.16 software, followed by further processing using the Origin 2019 software. The x-ray diffraction (XRD) measurements were carried out in a Malvern Panalytical Empyrean diffractometer with Cu Ka radiation (λ = 1.54 Å). The 0–2θ scan was carried out from 5° to 60° with a step size of 0.001°. The surface morphology of the perovskite films was examined using Jeol JSM-7900F scanning electron microscopy (SEM). The thickness of the perovskite films was measured using a Veeco Dektak 150 surface profilometer. The optical absorption spectra were obtained in transmission mode using a Cary 5000 UV–Vis–NIR spectrometer (Agilent Technologies, USA) equipped with the Cary WinUV 6.1 software. The top surface of the films was exposed to a constant illumination of 1 Sun and kept under ambient atmosphere with relative humidity (~50 ± 5%), and absorption spectra were measured at regular intervals. The current density–voltage (J–V) measurements were carried out under ambient conditions using a Keithley 2636 source meter unit and a xenon lamp-based solar simulator (ORIEL Sol2A ABA) after calibration by a reference solar cell provided by Newport. All the J–V measurements were performed using a scan speed of 40 mV/s. The external quantum efficiency (EQE) measurements were carried out to measure the photo-response as a function of wavelength, using a Benthams quantum efficiency system (Benthams/PVE300).

III. RESULTS

A. Phase segregation: Optical and structural studies

Figure 1(a) represents the absorption spectra of fresh perovskite thin films with composition CH₃NH₃Pb(IₓBr₁₋ₓ)₃, where x = 0.00, 0.25, 0.50, 0.75, and 1.00. The absorption spectra showed the expected monotonic decrease in the bandgap with increasing iodide content, which is in agreement with the literature. The color of the films also changes from dark brown (x = 1.00) to yellow (x = 0.00) with increasing Br content (Fig. S1). The thickness of the CH₃NH₃Pb(IₓBr₁₋ₓ)₃ films is listed in Table S1. For the synthesis of perovskite films, we used lead acetate trihydrate instead of conventional lead halide (PbI₂) as the lead source. In general, the lead halide-based perovskite materials require an anti-solvent treatment to produce a compact and crystalline perovskite film. However, the solubility of the organic precursor in the anti-solvent and the miscibility of anti-solvent with the host solvent of the perovskite precursor impact the quality of the final perovskite film. Other parameters, such as anti-solvent volume, dripping time, and even the choice of anti-solvent, can also affect the film quality. In addition, the anti-solvent treatment is not a scalable technique. Instead, the lead acetate trihydrate route is a one-step anti-solvent free spin-coating technique that can produce ultra-smooth and pinhole free high-quality films, and this technique can be easily transferred to roll-to-roll fabrication. The CH₃NH₃PbI₃ perovskite exists in a tetragonal phase at room temperature, and CH₃NH₃PbBr₂ exists in a pseudo-cubic phase, which is relatively more stable. Figures 1(b) and 1(c) represent the evolution of the absorption spectra of CH₃NH₃PbBr₃ (film 00) and CH₃NH₃PbI₃ (film 100) perovskite films that were kept in ambient atmosphere under 1 Sun illumination, respectively. Exposure to light leads to photobleaching of the perovskite films, as is seen in the spectra by the decrease in the optical density (O.D.) with increasing exposure time. Film 00 shows excellent stability over the full wavelength range for the first 30 min and a slight decrease in O.D. at short wavelengths (<400 nm) after 1 h of constant illumination [Fig. 1(b)]. Meanwhile, film 100 shows a decrement in O.D. at short wavelengths (<450 nm) after 30 min exposure and further decreases after 1 h of constant illumination [Fig. 1(c)]. However, there is no significant change observed at the absorption edge in both cases. On the contrary, CH₃NH₃PbI₃Br₂ (film 75), CH₃NH₃PbI₂Br₃ (film 50), and CH₃NH₃PbI₂Br₃Br (film 25) show clear photobleaching at the absorption edge under 1 Sun illumination, as shown in Figs. 1(d)–1(f), respectively. A decreased absorption of the sample with mixed-halide composition (film 50) in the wavelength range 600–640 nm and a simultaneous increased absorption at the longer wavelengths (640–680 nm) are observed [Fig. 1(e)]. This results in a less abrupt absorption edge, accompanied by the growth of a tail at longer wavelengths with increasing exposure time. These spectral changes suggest that under steady state illumination, an initially homogeneous mixed halide perovskite film forms local phases that are I-rich and Br-rich. This is in good agreement with the literature. A similar observation can be seen for film 75 [Fig. 1(d)], but phase segregation is less significant in comparison with film 50 [Fig. 1(e)]. It is worth noting...
that 25% of Br (film 75) helps in maintaining the absorption spectra at shorter wavelengths (<400 nm) intact for the first 30 min. In film 25, the exciton absorption band at 570 nm is blueshifted by 40 nm and a slight increase in absorption in the wavelength range 600–650 nm is observed after 1 h of constant illumination [Fig. 1(f)].

To validate the phase segregation in mixed-halide perovskite films, x-ray diffraction (XRD) is carried out on the films at regular intervals, while they were kept under 1 Sun illumination in ambient atmosphere (Fig. S2). The diffraction peak of the (110) plane is analyzed for all the films to understand the mechanism of photochemical degradation in mixed halide perovskite films and to correlate it with the degree of phase segregation. The original position of the (110) diffraction peak increases gradually with composition from 14.0° for sample 100° to 14.9° for sample 00 [Fig. S3(a)]. Films 00 and 100 do not show any shift in the (110) plane after illumination [Figs. S3(b) and S3(f), respectively]. The reduction in peak intensity is attributed to photobleaching of perovskite films. A small shift of 0.02° toward lower angles is observed for film 75 [Fig. S3(c)] upon degradation along with a broadening in the peak. The shift in the (110) peak position toward lower angles increases to 0.05° for film 50. An additional shoulder appeared at 14.80° for film 50 [Fig. S3(d)] after illumination, which suggests the formation of I-rich and Br-rich phases. However, a shift of 0.1° in the (110) peak position is observed toward higher angles for film 25 after illumination [Fig. S3(e)]. Hence, optical and structural studies suggest the phase segregation in mixed halide perovskites along with photobleaching, when they are illuminated under ambient conditions. It is observed that photobleaching is more severe in the case of mixed halide perovskites than for the pure halide-based perovskites. In order to understand the higher degree of photobleaching in mixed halide-based perovskites, it is important to be cognizant about the changes in chemical bonding and electronic structure of the mixed halide perovskites before and after degradation.

B. Chemical analyses

Perovskite films with five different compositions are characterized by XPS, after exposure to different conditions, as defined in the Introduction. The film composition is quantified by using survey spectra, yielding approximate atomic percentages of the elements present in the perovskite films under different degradation conditions (Figs. S5 and S6). Figure 2 represents the normalized ratio of X vs Pb (X = I or Br or sum of both) for all the five films under different degradation conditions. A small reduction in the X:Pb ratio (1:0.96) is found for films 100 and 00 under chemical degradation [Fig. 2(a)]. However, the X:Pb ratio decreases to 1:0.88 for film 100 and 1:0.91 for film 00 under photo-degradation. The ratio further reduced to 1:0.86 for film 100 and 1:0.89 for film 00 under photochemical degradation. It is found that air exposure (moisture) has a minor effect in the degradation process. Instead, photoinduced ion migration plays a pivotal role in the degradation of pure halide-based perovskite films. Film 00 shows relatively better stability than film 100, which is in accordance with optical and structural studies and the literature as well. Films 75 and 50 both show that the migration of Br⁻ is faster than that of I⁻ [Figs. 2(b) and 2(c)], which supports the shift of the XRD (100) plane toward smaller angles. However, both Br⁻ and I⁻ migrate significantly in the case of film 25 [Fig. 2(d)]. It is also observed that air exposure has a little effect on the chemical composition of pure halide perovskite, but it affects the chemical composition in mixed halide perovskites significantly. In addition, the ion migration is clearly more prominent in mixed halide perovskites than in pure halide perovskites, which could be related to the degree of phase segregation. For the reliability of the results,
FIG. 2. The X (I and Br) to Pb atomic ratios extracted from XPS survey scans for pure halide perovskites (a) CH$_3$NH$_3$PbI$_3$ (100) and CH$_3$NH$_3$PbBr$_3$ (00), and mixed-halide perovskites (b) 75, (c) 50, and (d) 25, under different degradation conditions: PH = photo-degradation, CH = chemical degradation, and PHCH = photochemical degradation. X = Br (green bar), X = I (brown bar), and X = I + Br (orange bar).

FIG. 3. C 1s core level spectra of films (a) 100 and (b) 00 under different degradation conditions. N 1s core level spectra of films (c) 100 and (d) 00 under different degradation conditions. Here, PH = photo-degradation, CH = chemical degradation, and PHCH = photochemical degradation.

The XPS experiments were conducted on two different perovskite samples (fabricated in different batches) for fresh and photochemical degraded films, and no significant difference was observed. The decrease in halide ions during photochemical degradation of mixed halide perovskites suggests the formation of PbX$_2$ on the surface.\textsuperscript{18,19}

Figures 3(a) and 3(b) represent the core level C 1s spectra of films 100 and 00 under different degradation conditions, respectively. Film 00 shows a single component peak at 286.3 eV, which is related to perovskite (C–NH$_2$). However, film 100 shows a broader peak containing a second component at 284.8 eV, which is attributed to carbon contamination (C–H or C–C) along with the component
Contamination during transfer of samples can be excluded because all fresh films were transferred from the N\textsubscript{2}-filled glovebox to the XPS chamber without any exposure to the ambient atmosphere. After exposure to ambient in the dark for 1 h (CH), a new component appeared at 284.8 eV for film 00, which was absent for the fresh film. It is found that the intensity of the component at 284.8 eV for film 100 increased in comparison with that for the fresh film. For photo-degradation (PH), the peak at 286.3 eV decreases in intensity (Figs. 3 and S7) for both pure films (100 and 00), which is attributed to the photoinduced degradation of the perovskite materials. For photochemical degradation (PHCH), a further reduction in the peak at 286.3 eV is observed, and simultaneously, an increase in the intensity of the peak at 284.8 eV is observed. To compensate for any surface charging effect, the core level C 1s (C–C or C–H bond) spectrum is shifted so that the peak maximum matches 284.8 eV and is then used as a reference to calibrate all the other spectra for each sample, by shifting the core level with the same energy difference. Figures 3(c) and 3(d) represent the core level N 1s spectra of the pure halide films 100 and 00, respectively. The peak positions of N 1s in samples 00 and 100 are at 401.9 and 402.7 eV, respectively. No significant shift in the N 1s peak position is observed for the pure halide films under any of the different degradation conditions. However, photoinduced degradation leads to a reduction in the N 1s peak intensity of the degraded films (Fig. S8).
FIG. 5. Pb 4f core level spectra of films (a) 100 and (b) 00 under different degradation conditions. (c) I 3d core level spectra of film 100 and (d) Br 3d core level spectra of film 00 under different conditions. Here, PH = photo-degradation, CH = chemical degradation, and PHCH = photochemical degradation.

Figures 4(a)–4(c) represent the core level C 1s spectra of mixed halide perovskite films 75, 50, and 25, respectively. Similar to film 100, all the mixed halide films show two peaks at 284.8 and 286.3 eV in the C 1s spectra. The effect of photoinduced degradation is more pronounced in film 25 [Figs. 4(c) and S7(e)]. The peak at 286.3 eV is diminished, and the C 1s spectra are dominated by the 284.8 eV peak. The extent of photoinduced degradation in film 50 is higher than that of the pure halide films (100 and 00) and mixed halide film 75, but lower than film 25 [Figs. 4(b) and S7(d)]. Similar to pure halide films (100 and 00), film 75 also does not show any significant shift in the peak position of N 1s spectra; however, it appears at a slightly different peak position of 402.6 eV and is shown in Fig. 4(d) [Fig. S8(c)]. The N 1s peak positions for fresh films 50 and 25 are 402.6 and 402.0 eV and are shown in Figs. 4(e) and 4(f), respectively. Both the films neither show any significant change in the shape of the spectra, nor any shift in the peak position under chemical degradation (CH). However, upon photo-degradation, both films show a broadening of the N 1s spectrum in comparison with the fresh films. The peak position of the N 1s spectrum under PH and PHCH degradation for films 50 and 25 shows a slight shift to 402.5 and 402.1 eV, respectively. However, the broadening in the spectrum results in a poor fit of the spectrum with $\chi^2 \leq 0.85$. It suggests convoluting the spectrum with two distinct components. A good fit to the spectrum with $\chi^2 \geq 0.95$ is obtained with two components at 402.4 and 402.7 eV for film 50 and at 402.0 and 402.7 eV for film 25. These two components can be attributed to different electronegativity surroundings in the I-rich and Br-rich environments. The peak positions and reduced $\chi^2$ values for the N 1s spectra for all the films under different degradation conditions are listed in Table S2. This result suggests that due to photoinduced phase segregation, the N 1s spectra show contributions from the I-rich and Br-rich phases. The higher binding energy N 1s component corresponds to MA in the I-rich phase, and the lower binding energy peak is associated with the Br-rich phase. The contribution at high binding energy becomes more pronounced in the N 1s spectra of photochemically degraded films. This is in correlation with the faster migration of Br$^-\text{in comparison with I}^-$. The core level Pb 4f spectrum for film 100 shown in Fig. 5(a) shows the spin–orbit split doublet Pb 4f$_{7/2}$ and Pb 4f$_{5/2}$. The separation between the doublet peaks is 4.88 eV, which is in good agreement with the literature. The fresh film 100 also shows an additional Pb feature at a binding energy of 1.8 eV below the main peak. This feature is attributed to uncoordinated metallic lead (Pb$^\text{0}$). The Pb$^\text{0}$ peak increases slightly under different degradation conditions. Interestingly, there is no change in the Pb 4f spectra of film 00 under different conditions, as is shown in Fig. 5(b). The halide spectra for the pure component films are shown in Fig. 5(c) (film 100) and Fig. 5(d) (film 00). Neither the I 3d spectrum for film 100 [Fig. 5(c)] nor the Br 3d spectrum for film 00 [Fig. 5(d)] is affected upon exposure to different degradation conditions. The Pb 4f spectra of the mixed halide films are shown in Fig. 6. Film 75, in analogy with film 100, has a small contribution of Pb$^\text{0}$ and shows a good stability in ambient, but a slight increase in the Pb$^\text{0}$ contribution upon exposure to light (PH and PHCH) [Fig. 6(a)]. Neither for films 50 and 25 could be seen any significant change in the Pb 4f spectra upon exposure to air in the dark [CH; Figs. 6(b)].
FIG. 6. Pb 4f core level spectra of mixed halide perovskite films (a) 75, (b) 50, and (c) 25 under different degradation conditions. Here, PH = photo-degradation, CH = chemical degradation, and PHCH = photochemical degradation.

However, upon exposure to light in N₂ (PH) and in air (PHCH), the Pb 4f spectrum of film 50 shows a shift of the Pb 4f doublet peaks toward a higher binding energy [Fig. 6(b)] and film 25 shows an even larger shift of the Pb 4f doublet peaks toward a higher binding energy than film 50 [Fig. 6(c)]. In addition, the Pb⁷⁺, which contributes strongly to the spectrum of the fresh 25 film, also increases under photo-degradation and photochemical degradation conditions. These shifts in the Pb 4f spectra form another clear indication of the formation of PbX₂ on the surface of films 25 and 25, despite having a higher bandgap than devices 100 and 75 [Fig. S12(b)]. However, a decrease in V₉₀ is observed for devices with composition 50 and 25, despite having a higher bandgap than devices 100 and 75 [Fig. S12(b)]. It is observed that the shape of the Br 3d and I 3d spectra for film 25 in comparison with film 50 (Fig. 7). It is observed that the photo-degradation and photochemical degradation [Figs. 7(a) and 7(b)]. This is attributed to the desorption of Br/I atoms under the influence of photons. Overall, the Pb 4f, Br 3d, and I 3d core level spectra suggest the formation of PbX₂ on the surface of the mixed halide films 50 and 25, while film 75 shows a good stability for all the core level spectra.

C. Photovoltaic (PV) performance and energetic landscape

In order to transfer the knowledge gained on the degradation of mixed halide perovskite films to their application in devices, perovskite solar cells (PSCs) were fabricated with an inverted (p-i-n) architecture [Fig. S12(a)]. Figure 8(a) represents the current density–voltage (J–V) characteristics of the pure and mixed halide PSCs under 1 Sun illumination. Table I shows the PV parameters of the five champion devices. The average PV parameters, including power conversion efficiency (PCE) and hysteresis index (HI), over eight devices are shown in Fig. S12. In general, the open-circuit voltage (V₉₀) of the PSC is directly proportional to the bandgap of the material. Here, the V₉₀ increases for devices with perovskite composition 75 in comparison with devices with the pure iodide composition 100, by increasing the Br content to 25% [Fig. S12(b)]. However, a decrease in V₉₀ is observed for devices with composition 50 and 25, despite having a higher bandgap than devices 100 and 75 [Fig. S12(b)]. It is in good agreement with reports in the literature and attributed to the phase segregation in mixed halide PSCs. Figure 8(b) represents the external quantum efficiency (EQE) spectra of the mixed halide PSCs. The EQE absorption edge shifts toward shorter wavelengths with increasing Br content in the film, which is in good correlation with the absorption spectra [Fig. 1(a)] and the observed decrease in the short-circuit current density (Jₚ₉₀) [Fig. S12(c)]. From the XPS analysis, it is quite evident that photo-induced phase segregation plays the dominant role in the material instability of mixed halide perovskite films. Hence, the devices were degraded for 1 h under PHCH condition only and the J–V characteristics under illumination were recorded immediately. A histogram in Fig. 8(c) shows the normalized PCE of the degraded devices under PHCH condition with respect to that of the fresh devices. It was found that device 00 (pure Br) was the most stable among all the devices, followed by devices 100 and 75. On the contrary, device 50 and 25 degraded completely after 1 h of constant 1 Sun illumination under ambient atmosphere. In order to understand the degradation mechanism in mixed halide PSCs (device 50 and 25), the energetic landscape was explored using UPS for fresh and PHCH films, and the results are shown in Fig. 8(d). It was found that the valence band (VB) onset is not much affected by changing the Br-to-I ratio for fresh films (Fig. S13). On the contrary, mixing of Br and I showed a significant effect on the position of the fermi level (Fig. S14). The fresh film 100 shows an n-type behavior, but an increase in the Br content results in the formation of p-type perovskite films. As a consequence of the change in the work function of the mixed-halide perovskite films by increasing the Br content, the valence band maximum (VBM) shift in the downward direction (away from the vacuum level). In addition to UPS, the VB spectra of all the fresh films were also measured by the XPS technique. The VB onset of fresh films
FIG. 7. Br 3d (a), (c), and (e) and I 3d (b), (d), and (f) core level spectra for films (a) and (b) 75, (c) and (d) 50, and (e) and (f) 25 under different degradation conditions. Here, PH = photo-degradation, CH = chemical degradation, and PHCH = photochemical degradation.

FIG. 8. (a) Illuminated current density–voltage (J–V) characteristics and (b) corresponding external quantum efficiency (EQE) spectra of perovskite solar cells based on CH₃NH₃Pb(IₓBr₁−ₓ)₃ , where x = 0.00, 0.25, 0.50, 0.75, and 1.00. (c) Histogram of the PCE values of degraded devices under PHCH condition, normalized by the PCE value of the corresponding fresh device. (d) Energetic landscape, derived from ultraviolet photoelectron spectroscopy (UPS), of fresh (solid spheres) and degraded (open circles) mixed-halide perovskite solar cells with different halide ratios.
<table>
<thead>
<tr>
<th>Device</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.06</td>
<td>22.37</td>
<td>0.74</td>
<td>17.55</td>
</tr>
<tr>
<td>75</td>
<td>1.17</td>
<td>18.20</td>
<td>0.77</td>
<td>16.39</td>
</tr>
<tr>
<td>50</td>
<td>1.05</td>
<td>13.46</td>
<td>0.68</td>
<td>9.61</td>
</tr>
<tr>
<td>25</td>
<td>1.04</td>
<td>10.95</td>
<td>0.36</td>
<td>4.10</td>
</tr>
<tr>
<td>00</td>
<td>1.32</td>
<td>6.39</td>
<td>0.56</td>
<td>4.72</td>
</tr>
</tbody>
</table>

The MAPbBr<sub>3</sub> (film 00) perovskite is known to be in a pseudo-cubic phase at room temperature. The methylammonium ion (MA) inside the PbBr<sub>6</sub> octahedral cage moves under illumination, which causes alteration of the Pb–Br bond length and also a deviation from the 90° Br–Pb–Br bond angles (or 180° Pb–Br–Pb bond angles). The interaction between the MA and PbBr<sub>6</sub> is through a weaker hydrogen bonding and is influenced by the bond angles and bond length between Pb–Br. The choice of halide in the perovskite structure decides the Pb–X bond length because it increases with increasing halide size. Mixing bulky I into pure Br based perovskite results in inhomogeneity in the bond angles and can lead to reduced bond strength. Under illumination, the weak hydrogen bond breaks and causes degradation. The decrease in counts is quite evident in the C 1s and N 1s core level spectra of mixed halide films (Figs. S7 and S8). The photobleaching is strongest for film 25, followed by film 50. The pure Br based perovskite film (film 00) shows least photo-degradation among all the films. The slight difference in the peak position in the N 1s spectra for mixed halide perovskite films with respect to pure halide films indicates the presence of different electronegative background/surroundings. The mixed-halide films also show two contributions from the I<sup>-</sup> rich and Br<sup>-</sup> rich phases in the N 1s spectra of degraded films (Fig. 4) and are in good correlation with the atomic composition ratios obtained from XPS (Fig. 2). From the Pb 4f XPS spectra, we have observed that the photoinduced segregation and anion migration under 1 Sun illumination result also into the formation of PbO on the perovskite film surface, which is known to be uncoordinated Pb and acts as a recombination center in the semiconductor (Figs. 5 and 6). Similar to other results, we find that film 25 shows a higher increase in PbO after degradation. In addition, mixed halide films 50 and 25 show shifts of the peak positions in the Pb 4f core level spectra toward a higher binding energy, which is in good agreement with the literature regarding the formation of PbO<sub>2</sub> on the perovskite surface. The Br 3d and I 3d core level spectra of degraded films 50 and 25 show a similar trend as the Pb 4f spectra. Film 75 shows a better photochemical stability than films 50 and 25. The 25% of Br in film 75 helps maintaining the stoichiometry under exposure to illumination in air and protect the perovskite from photochemical degradation. The photo-degradation also reduced in comparison with the pure iodine-based perovskite film 100. All the core level spectra and electronic
structure of film 75 do not show any significant shift in binding energy upon degradation. The pure Br-based perovskite film shows the highest photochemical stability among the five compositions. Our results suggest, in agreement with previous studies, that for a stable mixed halide perovskite film, the Br content in I-based perovskites should be less than 25% of the total anion concentration to prevent photoinduced segregation. The inclusion of Br (>25%) in the pure I-based perovskite results in photoinduced instability of the mixed halide perovskite films and highly affect the energetic landscape by the formation of barrier at the perovskite/charge transport layer interface, which finally hampers the device stability. This chemical and electronic structure study contributes with new insights into the instability of mixed halide perovskites under close to operating condition and correlates with the device instability.

V. CONCLUSION

In conclusion, this work describes a comparison of the degradation process in mixed-halide perovskites with pure halide perovskites. The chemical analysis reveals that exposure to the ambient air (moisture) has no major effect on degradation; however, photoinduced phase segregation and ion migration play a pivotal role in the degradation of mixed halide perovskites. This study represents the analyses of N 1s, in which contributions from I-rich and Br-rich domains can be distinguished, supporting the anion migration under exposure to light under ambient conditions (photochemical degradation). The effect of the Br-to-I ratio on the electronic structure of mixed halide perovskites is established with the UPS technique. The impact of photochemical degradation on the electronic structure of the mixed halide is also addressed to understand the device instability. This study also confirms that mixed halide perovskites containing more than 25% Br showed a stronger phase instability and it increases with increasing Br content in the film.

SUPPLEMENTARY MATERIAL

The supplementary material contains electronic images of perovskite films, XRD of fresh and degraded films, SEM of fresh and degraded films, and survey and core level XPS spectra for fresh and degraded films.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Shivam Singh: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Methodology (equal); Validation (equal); Visualization (lead); Writing – original draft (lead); Writing – review & editing (equal). Ellen Moons: Funding acquisition (lead); Methodology (supporting); Project administration (lead); Resources (lead); Supervision (lead); Validation (equal); Visualization (supporting); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES