

# Investigating the Effects of Chemical Gradients on Performance and Reliability within Perovskite Solar Cells with TOF-SIMS

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Time-of-flight secondary-ion mass spectrometry (TOF-SIMS), a powerful analytical technique sensitive to all components of perovskite solar cell (PSC) materials, can differentiate between the various organic species within a PSC absorber or a complete device stack. The ability to probe chemical gradients through the depth of a device (both organic and inorganic), with down to 100 nm lateral resolution, can lead to unique insights into the relationships between chemistry in the absorber bulk, at grain boundaries, and at interfaces as well as how they relate to changes in performance and/or stability. In this review, the technique is described; then, from the literature, several examples of how TOF-SIMS have been used to provide unique insight into PSC absorbers and devices are covered. Finally, the common artifacts that can be introduced if the data are improperly collected, as well as methods to mitigate these artifacts are discussed.

### 1. Introduction

Over the past decade, metal halide perovskite solar cells (PSCs) have made rapid gains in power conversion efficiency (PCE), starting from 3.8% in 2009<sup>[1,2]</sup> and steadily climbing to an astounding 25.2% in early 2019.<sup>[3]</sup> PSCs are now comparable to other leading solar PV materials such as cadmium telluride, copper indium gallium diselenide (CIGS), and silicon, which have record PCEs of 22.1%, 23.4%, and 26.1%, respectively.<sup>[3]</sup> Beyond improved PCE, PSCs are of particular interest because of their high defect tolerance, tunable bandgap, high absorption coefficient, long carrier diffusion length, and high carrier mobility, all of which are combined with facile solution-phase synthesis.<sup>[4–9]</sup> Perovskites also have promise as

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tandem devices, Tong et al. reported allperovskite tandem solar cells with PCE exceeding 25%, defect density reductions on the scale of an order of magnitude, carrier lifetimes over 1 µs, and diffusion lengths over 2.5 µm.<sup>[10]</sup> Despite valid concerns of PSC stability, recent studies inspire confidence in that area, as well. Christians et al. showed unencapsulated perovskite solar cells with PCE stability for more than 1000 h.[11] Lira-Cantú reported on encapsulated PSC device stability over 10 000 h.[12] Unlike traditional silicon PV material, perovskite crystals do not follow a two-interpenetrating facecentered cubic structure.<sup>[13]</sup> Rather, the term perovskite refers to a cubic crystal structure with the generalized chemical

formula, ABX<sub>3</sub>. The A-site cation is usually a large organic cation, most commonly methylammonium (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, or MA<sup>+</sup>) or formamidinium  $(CH(NH_2)_2^+, or FA^+)$ ; and increasingly, cesium<sup>+</sup>, rubidium<sup>+</sup>, potassium<sup>+</sup> and are used. The B-site cation is typically lead (Pb<sup>+</sup>), but more recently, tin (Sn<sup>+</sup>) is used as a substitute which aids in forming a lower-bandgap material for multijunction PSC applications. The X-site anion tends to be a halogen species, most commonly iodine-, although species like bromine<sup>-</sup>, chlorine<sup>-</sup>, and guanidinium thiocyanate<sup>-</sup> are of increasing interest as supplements to iodine due to stability improvements.<sup>[4,5,10,13-15]</sup> Historically, the most commonly studied PSCs are of the form methyl-ammonium lead iodide (MAPbI<sub>3</sub>). Despite the promise of PSCs, several barriers to broad commercial adoption remain. Key issues include unstable interfaces in PSC devices, solvent-exchange engineering, hysteresis and light soaking, narrow spectral absorption, and (perhaps) the need to reduce lead content.<sup>[4,5,12,13,16-20]</sup>

Attempts by the scientific community to address PSC stability through passivation of internal defects and interfaces have led to increasingly complex composition schemes and passivating additives. Many groups have studied PSC stability and proposed perovskite composition solutions, but the details of the fundamental degradation mechanisms are still difficult to remedy. The literature has identified moisture penetration into the lattice, oxidation, photo-induced reactions, temperature, and halogen diffusion, particularly at device surfaces and interfaces, as the most relevant degradation pathways.<sup>[4,5,13,17]</sup> Developing a robust toolkit of advanced characterization methods and techniques is crucial for further improvements in PSC technology. Other advanced characterization techniques routinely employed

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in the field include scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES)—which are covered elsewhere in this special issue–as well as time-of-flight secondary-ion mass spectrometry (TOF-SIMS), which is the subject of this review. To briefly compare TOF SIMS with the other ultra-high vacuum surface characterization techniques; XPS is useful to obtain information about chemical states at surfaces and at interfaces, information TOF-SIMS cannot provide. While AES can provide standardless quantified imaging and depth profiling of the inorganic components of PSCs with lateral resolution on the order of 10–15 nm, albeit with detection limits on the order of 0.1% (much higher than TOF-SIMS), and beam damage from the electron beam is a great concern in AES.

TOF-SIMS is a versatile ultra-high-vacuum characterization technique widely employed in surface and interface analysis assays. TOF-SIMS analysis can obtain high-resolution surface spectrometry, 2D imaging, depth profiling, and 3D tomography data. TOF-SIMS has excellent mass-resolution spectrometry ( $m/\Delta m = 10\ 000$ ), lateral-resolution capabilities on the order of 100 nm, and is capable of detection limits better than parts per million.<sup>[21,22]</sup> The instrument can measure secondary-ion species in either positive or negative polarity and has adjustable analysis and sputtering-beam energy and flux parameters that allow for tuning the measurement to obtain organic molecular information rather than the mostly organic fragments, which is common in XPS or AES depth profiling. For these reasons, TOF-SIMS is well suited for surface and interface analysis of PSC materials and devices.

In TOF-SIMS, a given analyte is bombarded with a pulsed, high-energy, focused beam of primary ions, typically with an ion energy up to 30 keV. Different ion beams can be used for analysis as well as sputtering and can include bismuth, cesium, argon, oxygen, or gallium. In addition, clustered ion sources of bismuth, argon, carbon, or gold can also be used. Incident primary ions penetrate the sample surface, which results in a collision cascade (interaction depth of no more than a few nanometers and typically sub-nanometer is common). The collision cascade causes sample atoms and molecules to be ejected into the vacuum, a small amount of which ( $\approx$ 1%) is emitted as charged secondary ions that can be sent to the detector using an extraction field on the order of tens of volts. The greater the energy of the analysis beam, the deeper the primary ions penetrate the sample; this also results in a large number of subsurface broken bonds, which is not ideal for analyzing organic species. Figure 1 shows a schematic example of the SIMS collision cascade, atom and molecule ejection, and primary-ion implantation phenomena. When combined with a high-flux, low-energy sputter beam (0.5-1 keV typical), depth profiling can be realized. More details on the basics of TOF-SIMS measurements will be covered in Section 2.

TOF-SIMS is becoming a more commonly used technique for PSC analysis, and several recent examples from the literature are given here. Li et al. reported on thermally induced degradation for inverted PSCs. Direct evidence of ion diffusion through the electron transport layer (ETL) to the silver (Ag)/phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) interface is presented using TOF-SIMS analysis. In particular, TOF-SIMS depth profiles were taken of two sets of model MAPbI<sub>3</sub> PSC





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**Figure 1.** An illustration of the SIMS primary-ion collision cascade that results in sample material being ejected from the first few monolayers of the sample surface due to the impact of the high-energy primary-ion beam. A small amount of the ejected material is charged, and the mass of these charged secondary ions can then be analyzed. The primary-ion beam impact also results in atomic mixing in the subsurface region due to breaking of bonds in the matrix (shown as the semi-transparent area below the ion impact area). The amount of this damage depends on the energy per incident atom and the beam flux. Reproduced with permission.<sup>[23]</sup> Copyright 2019, American Chemical Society.

samples before and after a 24 h thermal treatment at either 85 °C or 100 °C. The comparative depth profiles clearly show I<sup>-</sup> and MA<sup>+</sup> migration to the Ag/PCBM interface post-thermal exposure and to a greater degree as temperature increases.<sup>[24]</sup> Zhang et al. used TOF-SIMS to show light-soaking-induced Ianion and MA<sup>+</sup> cation migration to the ETL and hole transport layer (HTL), respectively.<sup>[16,25]</sup> Huang et al. utilized TOF-SIMS to elucidate that a quasi-2D (2.5D) perovskite layer between the PSC film and a Spiro HTL can reduce iodine migration to the spiro interface, which significantly improves operational stability.<sup>[26]</sup> Li et al. studied the phenomenon of extrinsic ion migration in PSCs. Li and colleagues showed TOF-SIMS data suggesting Li<sup>+</sup> migration from lithium-doped spiro-OMeTAD HTL to the TiO<sub>2</sub> ETL. The Li<sup>+</sup> migration was found to boost open-circuit voltage ( $V_{oc}$ ), fill factor (FF), and carrier injection from the perovskite layer to the ETL. However, extrinsic ion migration was also found to contribute to current densityvoltage (JV)-curve hysteresis.<sup>[9]</sup> Domanski et. al. utilized TOF-SIMS depth profiling and 3D tomography to show significant migration of the gold contact through the HTL due to elevated temperatures up to 70 °C.[27] Lee et. al. utilized TOF-SIMS to reveal dimethylamine in PSC films, which they suggested was due to a transamidation of methylamine (MA) with residual dimethylformamide (DMF) in the film.<sup>[28]</sup> In important early work, Akbuhlatov et. al. used TOF-SIMS profiling to show that significant MA and Iodine diffuse into the commonly used (at the time) c60-PCBM ETL after illumination, resulting in degradation of the MAPbI3, and suggested the community migrate to using different ETL materials.<sup>[29]</sup> Lin et al. studied moisture degradation mechanisms for PSC via in situ TOF-SIMS. Specifically, moisture diffusion was tracked into the model MAPbI<sub>3</sub> perovskite lattice on a mesoporous TiO<sub>2</sub> layer. Lin and colleagues developed a novel method for tracking and measuring moisture diffusion by using D<sub>2</sub>O (heavy water) rather than H<sub>2</sub>O to distinguish extrinsic moisture diffusion into the lattice from moisture native to the perovskite film from fabrication. Using in situ depth-profile measurements and corresponding 3D tomography figures, chemical information was captured and reveals a successive degradation of the MA<sup>+</sup> organic cation via proton exchange with D<sub>2</sub>O. The protonexchange mechanism leads to the formation of highly volatile MAs, which evaporate from the lattice. Moisture-induced degradation begins at the top of the film and in only 3 days or so, it completely penetrates the entire perovskite film. By day 5 of D<sub>2</sub>O exposure, all of the MA organic species and accompanying MA derivatives have been completely expelled from the lattice, leaving only PbI<sub>2</sub> and TiO<sub>2</sub> in a collapsed perovskite/ TiO<sub>2</sub> structure.<sup>[18]</sup> Matteocci et al. studied the effect of deposition methods and conditions on interfacial and compositional properties of PSC. They used TOF-SIMS depth profile and 2D imaging data to propose that gold and iodine diffusion and interface quality are strongly affected by the conversion process and environmental conditions during the fabrication of perovskite films. Vapor-assisted solution deposition (VASP) displayed the sharpest interfaces. However, 2D imaging data showed that VASP also promotes gold inhomogeneity and localized pinhole diffusion through the Au/spiro-OMeTAD interface. Depth profile data show significant I<sup>-</sup> diffusion into the mesoporous TiO<sub>2</sub> ETL layer for one-step deposition. For the VASP conversion process, perovskite crystallization improves as a function of depth from the spiro-OMeTAD layer to the TiO<sub>2</sub> layer. Two-step deposition processes that underwent an MAI dip conversion process had the highest PCE and most homogeneous perovskite crystallization. These results are explained by highlighting that non-dip conversion processes do not fill defects in the HTL and ETL layers as well as MAI dip conversion processes.<sup>[30]</sup> The two-step perovskite deposition method (not for PV applications) was first reported by Mitzi et al. in 1997.<sup>[31]</sup>

While TOF-SIMS can yield a wealth of insight into PSC materials and devices, it is often best to leverage it with additional complimentary characterization methods (many of which are covered elsewhere in this special issue) to understand fully a given performance or degradation mechanism, or to further understand beam-damage artifacts from TOF-SIMS with complimentary analysis. TOF-SIMS data can provide insight into interface composition, chemical gradients and spatial distributions through imaging, but it cannot say anything about the structure and is difficult to interpret bonding information from TOF-SIMS data. That is why TOF-SIMS is often combined with XRD, SEM, XPS as well as other analytical techniques to paint a more complete picture than TOF-SIMS alone could do. While many studies listed in the literature review earlier utilize such combined approaches a few examples which highlight such complimentary studies are listed here.

In the early work Matteocci et. al utilized XPS, TOF-SIMS and Scanning transmission electron microscopy analysis to



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investigate correlations in the structure and composition to performance in PSC materials fabricated from four different deposition methods. It was found that performance correlated strongly with the quality of the interface between the PSC and the mesoporous TiO<sub>2</sub>, evidence for iodine migration was also shown.<sup>[30]</sup> Boldreva et. al used optical absorption data, PCE data and XPS data in combination with TOF-SIMS to investigate interface degradation effects in five different organic charge transport layers, and they found in most cases degradation at the MAPbI<sub>3</sub>/CTL interface preceded MAPbI<sub>3</sub> degredation.<sup>[32]</sup> Tong et. al. utilized an array of advanced characterization methods, including TOF-SIMS to understand the mechanisms behind the dramatically improved performance when utilizing a guandinium thiocyante additive in a low-bandgap Sn-Pb perosykites, which enabled carrier liftetimes of >1 us and 25% efficient four-terminal all perovskite tandem devices.<sup>[10]</sup> Busby et. al utilized XPS and TOF-SIMS depth profiling to elucidate the performance and stability improvements when graphene nanoflakes are incorporated into the mesoporous TiO<sub>2</sub> ETL. It was shown that the graphene improved the electron transport from the MAPbI<sub>3</sub> to the mesoporous TiO<sub>2</sub>. TOF-SIMS and XPS were also utilized in this study to show the increase in PbI and PbO at the interface upon degradation, as well as migration of gold and iodide throughout the entire device stack.<sup>[33]</sup> Ralaiarisoa et. al. performed a study utilizing TOF-SIMS tomography, grazing incidence XRD, and XPS to investigate changes in structure and composition in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> films before, during, and after a crystallization anneal. They showed that in the early stages of annealing chlorine-rich domains are present, after full crystallization of the perovskite phase the chlorine has migrated toward the conducting polymer substrate. XPS showed an increase in n-type character as the film became more fully crystallized into the perovskite phase.[34]

TOF-SIMS has also provided useful insight in the field of perovskite quantum dots (QDs), to name just a few examples; Sanehira et al. used TOF-SIMS to understand the role of a formamidinium iodide salt post-treatment. It was determined that formamidinium was between CsPbI<sub>3</sub> QDs and resulted in a record efficiency of 13.43% for a QD film.<sup>[35]</sup> TOF-SIMS was used by Wheeler et al. in combination with many other advanced characterization techniques to uncover the mechanism of this FAI post-treatment and how FA replaces oleylammonium bound to the QD surfaces.<sup>[36]</sup> Zhao et al. used TOF-SIMS to demonstrate the robust interface between two distinct layers of CsPbI<sub>3</sub> QDs and Cs<sub>0.25</sub>FA<sub>0.75</sub>PbI<sub>3</sub> QDs. The interface improves charge separation and collection, but is predicated on a stable interface which was well resolved with TOF-SIMS.<sup>[37]</sup>

TOF-SIMS has long been used in the traditional semiconductor industry to measure low concentration inorganic impurities.<sup>[38]</sup> However, for use in organic and hybrid organicinorganic samples such as PSCs, carefully considered and optimized analysis and sputtering-beam parameters are essential for high-quality SIMS data.<sup>[39]</sup> Early work on optimizing analysis beam parameters for TOF-SIMS characterization of organic films was carried out by Brison and Castner, where they evaluated a single-beam and dual-beam approach. Furthermore, they developed standardized metrics to quantitatively investigate the relative significance of the analysis and sputtering-beam fluence on beam-damage accumulation and the efficiency with which the sputtering beam removes bulk material, damaged by the analysis beam. The authors conclude that for dual-beam analysis, which is the standard practice, the analysis-beam fluence is the most significant source of chemical damage in the film. Moreover, it was shown that for both the analysis and sputtering beam, the use of a gas cluster ion beam (GCIB) contributed to a reduction in beam-damage accumulation. For the analysis beam, the GCIB causes the energy of the analysis beam to be distributed throughout the cluster, resulting in a shallower analysis-beam damage depth. For the sputtering beam, GCIB causes a greater sputter yield and thus, greater removal of the damaged surface.<sup>[39]</sup> Mahoney extensively investigated cluster SIMS characterization of organic and polymer materials and also found that cluster sources for analysis and sputtering beams significantly reduced beam damage and improved the retention of organic molecular information due to the relatively low energy per atom.<sup>[40]</sup> Winograd described the upside that cluster SIMS offers for 3D tomography data acquisition and, more specifically, the characteristic properties of reduced topographic roughening, enhanced ion yields for large atomic-mass species, minimal beam damage, and good depth resolution.<sup>[22]</sup> Wang et al. reported on advantages of argon GCIB analysis beams for insulating inorganic materials such as a perovskite oxide thin film. Generally, surface or interface charging can be averted with a compensating beam of electrons from a flood gun, but this becomes ineffective at high sputtering rates. Wang and colleagues found that an argon GCIB analysis beam resulted in less surface charging, strong signal intensity, high sputtering rates, and good mass resolution for perovskite oxide thin films.<sup>[38]</sup> This work has potentially significant applications for characterizing PSC architectures with native oxide and passivation layers.<sup>[41–43]</sup>

In the past work, Harvey et al. reported on best practices for TOF-SIMS characterization of PSCs, in particular, for interfacial studies of PSC devices, which is an increasingly important area of research in the PSC community. The significance of the matrix effect in TOF-SIMS analysis was discussed; the matrix refers to the bulk material and the matrix effect refers to the dependence of sputter yield and ionization probability on the matrix for a given secondary ion. It was found that the ideal analysis-beam parameters to avoid beam damage and fragmentation are a 30 keV Bi<sub>3</sub><sup>+</sup> beam.<sup>[44]</sup> In a more recent work, Harvey et al. reported on a beam-damage artifact commonly observed in the literature of TOF-SIMS depth profiles of PSC, manifested by a gradient in the organic cation.<sup>[9,11,16,20,24,30,44]</sup> After observing this gradient, a depth profile was performed starting from the buried PSC/transparent conducting oxide (TCO) interface, which resulted in the same negative gradient, thus proving that this gradient is an artifact due to beam damage when profiling. This work will be discussed in detail in Section 3.1.<sup>[23]</sup> Wehbe et al. completed a complimentary study including XPS and TOF-SIMS to investigate the advantages of using lowenergy Cs<sup>+</sup> as a sputtering source for TOF-SIMS characterization of non-PV organic samples, where it was shown that a reaction can occur between the implanted cesium and organic species, which can enhance the negative SIMS ion yield for those species due to a charge transfer mechanism from the implanted cesium to the organic species.<sup>[45]</sup> Xu et al. used principle component analysis to identify signatures in TOF-SIMS

data associated with degradation products due to exposure to moisture.<sup>[46]</sup> Noël et al. investigated monatomic (oxygen and cesium) and GCIB sputtering-beam conditions for TOF-SIMS analysis of perovskite films and devices. Noël and colleagues found  $Cs^+$  at 500 eV and  $Ar_{500}^+$  at 20 keV (40 eV per atom) to be the optimal sputtering-beam conditions for monatomic and GCIB, respectively.<sup>[47]</sup> In addition, Noël et. al. recently quantified the depth resolution of 500 eV Cs sputter beams when profiling organic materials like PSCs, and it was shown that the depth resolution can be as low at 4 nm for a 300 nm deep depth profile. It was also noted that the depth resolution is drastically improved when utilizing the newer Bi<sub>3</sub><sup>+</sup> cluster for the primary ion beam compared to Ga<sup>+</sup>. It was also shown that the fluence of the primary ion beam critically influences the depth resolution, even though its fluence is typically 5 orders of magnitude lower than that of the sputter beam.<sup>[48]</sup>

The review of the literature that was covered here contains work that has reported on prevalent measurement artifacts, optimal measurement conditions, and early applications or novel techniques related to TOF-SIMS analysis of PSC materials. As the PSC field has realized the powerful insight TOF-SIMS can yield in this materials system, TOF-SIMS data is becoming more commonly seen in the literature, and there are number of publications within the last year which utilize TOF-SIMS which were not otherwise discussed in detail in this review of the literature.<sup>[49–60]</sup> In this review article, we show examples of the basic types of data that can be obtained from TOF-SIMS analysis of PSC materials, and we also summarize updated best practices to identify and avoid TOF-SIMS measurement artifacts such as beam-damage accumulation, organic molecule fragmentation, and preferential sputtering.

## 2. TOF-SIMS Fundamentals

TOF-SIMS is a surface-sensitive mass spectrometry analytical technique, where a high-energy ion beam (typically 30 keV) is used to bombard the sample surface in high vacuum. The primary-ion beam impact causes a collision cascade and a breaking of bonds in the material, which can lead to the ejection of atoms and molecules from the near-surface region, as illustrated in Figure 1. The depth of altered material depends on the ion-beam energy as well as the bond strength of the material being probed. A small amount of the ejected material (<1%) is charged and the mass of these charged secondary ions can be analyzed with very high accuracy and sensitivity. Detection limits of sub ppm or even to ppb level are not uncommon in SIMS, and a mass resolution ( $m/\Delta m$ ) of greater than 10 000 can be easily achieved with TOF-SIMS.

The primary-ion beam impact does remove material from the sample, but it is not doing bulk sputtering. The primary-ion beam impact removes a small fraction of atoms or molecules from the near-surface region of the sample. When combined with a second lower energy ion source for bulk sputtering, depth profiling can be realized. Because the energy of the sputter beam is typically 1 keV or less, the damage depth is much lower than that from the primary beam, even while bulk sputtering is achieved due to much higher ion dosage. The flux of primary ions incident on the sample is referred to as the dose density, and this can critically affect the amount of beam damage observed when profiling, as well as the depth resolution, even though the dose density is orders of magnitude lower than the sputter beam dose density.<sup>[23,39,40,47,48]</sup> The depth resolution refers to the apparent thickness of an interface when depth profiling, this can influenced by many factors including surface roughness, interface roughness, beam energies, etc.<sup>[47,48]</sup> While many of these potential artifacts can be equaled out by analyzing a set of samples under identical conditions, it is important to try and minimize them whenever possible and keep these artifacts in mind when interpreting data.

SIMS is not without its limitations; the main limitation is that the relationship between intensity and concentration is complex. The SIMS intensity equation is shown in Equation (1).

$$i_{\rm A}^{\rm S} = I^{\rm P} Y \alpha_{\rm A} \eta_{\rm A} \theta_{\rm A} X_{\rm A} \tag{1}$$

where the SIMS intensity  $(i_A^s)$  is directly related to the primaryion beam current ( $I^p$ ), sputter yield of a given species (Y), ionization probability of the measured species ( $\alpha_A$ ), transmission efficiency of the detector ( $\eta_A$ ), isotopic abundance of the measured species ( $\theta_A$ ), and the fractional concentration of the measured species in the sample ( $X_A$ ). SIMS intensity is often incorrectly confused with concentration. Although the two are related, they are distinctly different, and this relationship makes quantification of SIMS data rather difficult.

As discussed in the previous works by Harvey et al.,<sup>[23,44]</sup> the intensity is strongly affected by the SIMS ion yield, which is influenced by the electronegativity of an atom or ion, as well as the surrounding material in the sample (the SIMS matrix effect). This means that SIMS intensity is not directly related to concentration when comparing intensity between two different atoms or molecules, that is, a SIMS signal for sodium (Na<sup>+</sup>) may exceed that of iodine (I<sup>+</sup>) when profiling in positive polarity, even though iodine is present at much higher concentration. However, even with this limitation, relative changes in SIMS intensity through the film/device thickness, or between samples of similar composition within a sample set can yield insightful information about the chemistry within the PSC material or device. Although SIMS excels at detecting small amounts of impurities in a matrix of different composition, SIMS signals when concentrations exceed  $\approx 0.1\%$  in a sample can be influenced by a change of the ion yield due to the differing matrix compositions upon alloying, and comparing signals at high concentrations can be error-prone. In such cases, other standardless techniques such as photoemission or Auger depth profiling may be useful; however, with these techniques, it can be difficult to distinguish between different organic cations, which is not an issue with TOF-SIMS.

## 3. Examples of TOF SIMS Data

#### 3.1. Depth Profiling

TOF-SIMS can provide unique information about the uniformity of both the inorganic and organic constituents through the depth of a PSC film or device, and how the cation gradients change upon aging. As the field trends toward





**Figure 2.** TOF-SIMS depth profile of formamidinium for two films of different composition, which underwent identical post-deposition processing, the carbon-13FA ( $^{13}$ CH(NH<sub>2</sub>)<sub>2</sub>) signal is shown. The large difference in the FA profiles through the film thickness illustrates how simply using the precursor bath chemistry as a proxy for film composition fails to capture actual film properties that would relate to the cation distribution in the film. Reproduced with permission.<sup>[44]</sup> Copyright 2018, American Chemical Society.

more complex compositions and moves toward the more common use of passivating additives at low concentration, TOF-SIMS can step in to provide critical insight about chemical distributions of all components and additives though the film/ device thickness which is not captured by the common practice in the field of simply quoting the precursor concentration used for spin coating the PSC film and using that as a proxy for final film composition. The importance of this point is illustrated in **Figure 2**, where the formamidinium profile for films made from two slightly different bath compositions is shown. There is a drastically different FA distribution for the two films, which could significantly affect device performance or reliability and could be erroneously attributed to the simple change of ink composition without the insight into the cation gradients provided by the TOF-SIMS depth profiling.

There are many factors to consider when depth-profiling PSC materials, and beam damage of the organic constituents from the 30 keV primary-ion beam is of paramount importance. The subsurface damaged region from a primary-ion beam impact depends on the energy per incident ion, and the damage depth and molecular ion yield for several common ion sources is schematically shown in **Figure 3**. After an analysis cycle, the SIMS sputtering beam removes bulk material from the analysis area. The sputtering beam is low energy and high flux, which results in shallow damage depth, but significantly more sample material ejection than the analysis beam due to higher flux. After bulk sputtering, the process repeats, and successive measurements are taken below the original surface,

generating a depth profile through the sample. In PSC materials, there is a higher propensity for beam damage due to the organic components of the material. When using a single-atom bismuth ion beam at 30 keV ( $Bi_1^+$  beam at left in Figure 3), the 30 keV bismuth ion has a deep damage depth and the high impact energy results in a large amount of subsurface broken bonds, leading to a low yield (thus low intensity) for molecular organic species such as MA or FA.

When a three-atom 30 keV bismuth cluster is used for the ion source (Bi<sub>3</sub><sup>+</sup> beam at right in Figure 3), the energy per incident ion is only 10 keV. So, the damage depth ( $d_1$  in Figure 3) is much lower than with  $Bi_1^+$  or  $Ga_1^+$  and the yield is much higher for molecular organic species.<sup>[48]</sup> This can be taken to an extreme with an argon GCIB source, where a cluster of argon atoms (500-3000 atom clusters possible) with a cluster energy of 1.5–20 keV can be used for both sputtering and analysis. The energy per incident atom can be as low as several electron-volts per atom, so the damage depth is very low and the yield for molecular organic species is very high; however, the damaged area ( $A_d$  in Figure 3) is also the largest.<sup>[39,47]</sup> Interestingly, the flux of the primary ion beam critically influences the depth resolution when profiling with 500 eV Cs<sup>+</sup>, even though the flux of the sputter beam can be as large as 5 orders of magnitude larger than that of the primary ion beam.<sup>[48]</sup>

Harvey et al. investigated beam damage during TOF-SIMS depth profiling in detail by cleaving PSC films at the back glass/TCO interface so that profiling could be conducted on the same sample both from the front and back of the device. The results, shown in **Figure 4**A, show that a similar gradient in the organic cation is observed in both cases. This indicates that the slight gradient in the organic cation through the film thickness is a beam-damage artifact that was present in prior published works and is also seen elsewhere in the literature.<sup>[23]</sup> The



**Figure 3.** Illustration of some of the concepts related to beam damage when depth-profiling molecular organic species. The relative depth of the damaged layer ( $d_1$ ) due to the breaking of subsurface bonds from a primary-ion beam impact and its collision cascade is shown for different primary-ion beams. The 30 keV bismuth single-ion beam (at left) has the deepest damage depth; the argon cluster beam (middle) has the least damage depth; and the Bi<sub>3</sub><sup>+</sup> ion beam (which is typically employed for perovskite depth profiling) has a damage depth between the other two ion beams. The damaged area ( $A_d$ ) is inversely proportional to the damage depth  $d_1$ , and the ion yield for molecular organics (proportional to the signal measured) goes in order  $Ar_n^+ > Bi_3^+ > Bi_1^+$ . The material removed from one theoretical sputter cycle depth  $d_2$ . The figure was created from the concepts covered in detail in Brison et al.<sup>[39]</sup> and is reproduced with permission.<sup>[23]</sup> Copyright 2019, American Chemical Society.





**Figure 4.** A) Methylammonium depth profiles for standard (frontside) depth profile, as well as an MA profile from the back of the film to the front, prepared through a sample-cleaving technique. The similar MA gradient in both profiles proves that this organic gradient is a measurement artifact. B) Optimized MA and FA profiles when using a 1 keV oxygen sputter beam (solid lines), as well as FA and MA profiles using a GCIB (dotted lines). The artifact seen in A is significantly lessened in the 1 keV oxygen data and appears completely absent in the GCIB profiles. For FA the carbon-13FA ( $^{13}$ CH(NH<sub>2</sub>)<sub>2</sub>) signal is shown, and for MA the CH<sub>3</sub>NH<sub>3</sub> signal is shown. Data replotted from that also shown in Harvey et al.<sup>[23]</sup> and is reproduced with permission.<sup>[23]</sup> Copyright 2019, American Chemical Society.

beam damage in this case was due to over-sampling with the primary-ion beam, because not enough material was removed in each sputter cycle to remove all the damage to the subsurface organic constituents from each primary-ion beam impact. This resulted in an accumulation of damage in the film and a continually decreasing organic cation signal when profiling, which was not reflective of the actual organic cation distribution in the film. This damage could be mitigated in two ways, both illustrated in Figure 4B. By reducing the data density (achieved through increasing the sputter time between primary-ion beam impacts), most of the damage from the primary beam could be removed during each sputter cycle and a less severe gradient is noted in the organic cation signals when using a 1 keV Cs sputter beam (solid lines in Figure 4B). Note that Noël et. al. determined 500 eV Cs to be ideal for profiling PSC materials due to the low penetration depth, however 1 keV is the lowest energy the sputter hardware can achieve on the NREL TOF-SIMS.<sup>[47,48]</sup> In addition, by changing the sputter hardware to use a GCIB source and using optimized GCIB conditions of 40 eV per atom as reported by Nöel et. al.,[47] the depth profile of the organic cations are constant through the entire film thickness and appear to show little to no beam-damage artifacts (dotted lines in Figure 4B).<sup>[23]</sup>

The specifics of current best practices for minimized beam damage to the organic cations while profiling were discussed in Harvey et al.,<sup>[23,44]</sup> as well as in the works of Noël<sup>[47,48]</sup> and are briefly repeated here for clarity.

- 1) A  $Bi_3{}^+$  primary-ion beam is used, and the dose density is  $1\times 10^{11} ions~cm^{-2}$  or less (50  $\times$  50  $\mu m$  analysis area is common).
- 2) Profiling is completed in non-interlaced mode to separate the analysis the sputter cycles, and so the sputter interval can be tailored to remove beam damage from the primary ion beam and to limit the number primary-ion beam-impact cycles, which can lead to damage accumulation.

- 3) A gas cluster ion source is preferred for sputtering if available, and an energy of 40 eV per atom is ideal (e.g., 500 atom cluster size at 20 keV beam energy).<sup>[47]</sup>
- 4) A sputter-gun energy of 1 keV or below or as close to that as achievable with the available sputter hardware ( $\approx$ 5–10 nA current) is used for cesium or oxygen sputtering if a GCIB is not available.<sup>[48]</sup> A 150 × 150 µm sputtered area is typically chosen, this can be altered to larger areas to influence the data density in a profile.
- 5) It is suggested that the sputter time per measurement cycle be varied by up to a factor 10× from the suspected idealized measurement conditions to check for damage accumulation artifacts, as shown in Figure 4.
- 6) Detector saturation should be avoided. This can usually be mitigated through following secondary ion clusters (e.g., I<sub>2</sub><sup>-</sup> when I<sup>-</sup> is saturated), lower abundance stable isotopes (e.g., <sup>204</sup>Pb<sup>+</sup> instead of <sup>208</sup>Pb<sup>+</sup>), or the carbon-13 analog for organic species which are saturated, (e.g., Carbon-13FA (<sup>13</sup>CH(NH<sub>2</sub>)<sub>2</sub>) for FA CH(NH<sub>2</sub>)<sub>2</sub>)).

The field of TOF-SIMS depth profiling is constantly evolving, and "best practice" measurement conditions will likely change over time. The conditions discussed earlier are intended to reduce beam damage in the organic cation signals when depthprofiling a single perovskite absorber layer. These conditions may also work well for complete devices or tandems. But the situation becomes more complex when considering multilayer stacks, and it is in the researcher's best interest to regularly search the literature in this area of technique development. In addition, researchers are recommended to perform measurements under different conditions and assess the degree in which measurement artifacts are altered in their system.

Regarding this point, it is impossible to remove all artifacts from a SIMS measurement because they result from ion-beam/ sample interactions that are inherent to the SIMS process. However, one can often find conditions where the artifacts



are negligible or do not greatly influence the data. It is recommended that researchers compare a set of samples (e.g., samples A, B, C, D) where some process variable is systematically varied (e.g., processing temperature, additive content, or fresh vs aged). One can then collect depth profiles on this sample set under identical measurement conditions (ideally at the same time). Thus, the artifacts that are present can be assumed to be identical in all profiles. Then the data can be used to compare relative changes in the profiles across the sample set and investigate the changes in the process variable on the material. Even within data from such an idealized sample set as described earlier, one cannot forget to keep general depth profile related artifacts in mind when interpreting the data. These include (but are not limited to); taking changes in the matrix composition across the sample set into account (which may change apparent signals without actual changes in concentration due to the SIMS matrix effect), depth resolution artifacts on the data (which may smear out interfaces in multilayer stacks), and convolution of data from multilayer stacks (measurement parameters may only be optimized for one layer in a stack).

One limitation of SIMS techniques, in general, is measurement polarity. Figure 1 showed a SIMS primary-ion beam impact, which results in ejection of sample material into vacuum. Most of this material is sputtered neutrals (>99% typically); the remaining >1% of sputtered material is charged secondary ions, which will be either positively or negatively charged. An extraction field is used to accelerate the charged secondary ions into the detector, so one must set up the instrument to look for either positive or negative species. This means that in certain cases, two separate measurements may be needed. Most species of interest for PSC materials show up best in positive measurement polarity. The exception is the highly electronegative halogen species. Successful application of an older SIMS methodology to PSC materials was recently reported where one sputters with a cesium ion beam in positive measurement polarity; this allows for monitoring of typical signals for FA, MA, Pb, etc. that ionize well in positive polarity, as well as significant enhancement of the halide ion signals when monitoring clusters of the halide ions plus cesium from the implantation due to sputtering.<sup>[23]</sup> In Figure 5, an increased sensitivity of 4 orders of magnitude is observed when monitoring the Cs<sub>2</sub>Br<sup>+</sup> cluster compared to just the Br<sup>+</sup> signal. Unfortunately, using a cesium beam for sputtering makes the interpretation of a cesium profile in the PSC material itself problematic. In those cases, where accurate information about the Cs profile in the film is needed, it is likely best to use a GCIB if available or an oxygen ion beam for depth profiling.

Detector saturation and dynamic range is a limitation of SIMS. Most standard TOF-SIMS instruments have 5 orders of magnitude of dynamic range, although that can be increased several more orders of magnitude with new extended dynamic-range analyzer hardware available from some TOF-SIMS manufacturers. While greater detail about detector saturation when profiling PSC materials is discussed in prior work, in general if saturation is an issue, one can look at higher-order clusters of the same species that have lower intensity. For example, Cs<sup>+</sup> is very electropositive and is often saturated in positive polarity; so following  $Cs_2^+$  or  $Cs_3^+$  clusters avoids this issue. The same is true for the halogen ions in negative polarity:  $I_2^-$  and  $I_3^-$ 





**Figure 5.** TOF-SIMS depth profiling showing the great enhancement of halide ions I and Br when using the MCs<sup>+</sup> profiling method. An improvement of over 4 orders of magnitude can be seen when comparing the Br<sup>+</sup> signal to the Cs<sub>2</sub>Br<sup>+</sup> secondary-ion cluster. The Cs<sub>2</sub>I<sup>+</sup> cluster is not shown because it was so high in intensity that it severely saturated the detector at  $10^5$  counts. Other higher-order clusters are shown because they can be used to avoid detector saturation, if present. Data replotted from that also shown in Harvey et al.<sup>[23]</sup> and are reproduced with permission.<sup>[23]</sup> Copyright 2019, American Chemical Society.

clusters usually avoid saturation. For organic species which are saturated one can follow instead the carbon thirteen analog, for example, carbon-13FA (<sup>13</sup>CH(NH<sub>2</sub>)<sub>2</sub>) for FA CH(NH<sub>2</sub>)<sub>2</sub>.<sup>[44]</sup>

#### 3.2. Imaging and 3D Tomography

The last few years in the PSC research field have seen a surge in the use of additives at relatively small concentration for a variety of reasons including encouraging grain growth, passivation of defects in the absorber bulk and/or at surface/interfaces in the device, and tuning interface energetics, to name several.<sup>[61-64]</sup> The TOF-SIMS instrument can be tuned for highresolution imaging (>100 nm lateral resolution possible), and with its inherent ability to easily distinguish between different organic species, high-resolution imaging can be used to observe the distribution of these additives in the film. For example, it can be seen whether the additive is uniformly distributed, or whether it tends to segregate at the grain boundaries in high concentrations, which could suggest a grain-boundary passivating role in the material. While better than 100 nm lateral resolution is possible to achieve in ideal conditions, a lateral resolution of a few-hundred nanometers is more common and depends on the quality of focus and the specifics of the sample (roughness, etc.). Figure 6A shows an example of an image of a cyanate signal (SCN<sup>-</sup>), which is prevalent at grain boundaries after a lead-thiocyanate additive was used to improve grain growth.<sup>[44]</sup> Figure 6B shows the guanidinium signal for a film with much smaller grain size, where at low concentration the





**Figure 6.** TOF-SIMS images of different passivating additives. A) TOF-SIMS 2D image of a lead thiocyanate passivating additive at the grain boundaries (SCN<sup>-</sup> signal shown).<sup>[44]</sup> B) 2D image of guanidinium signal at the grain boundaries at low guanidinium loading.<sup>[10]</sup> The scale at the right of each image is the intensity normalized to total counts. Figure 6A: Reproduced with permission.<sup>[44]</sup> Copyright 2018, American Chemical Society. Figure 6B: Reproduced with permission.<sup>[10]</sup> Copyright 2019, American Association for the Advancement of Science.

guanidinium additive is mostly present at grain boundaries; at higher loading, the guanidinium is also noted in the grain interiors (not shown). The guanidinium thiocyanate additive in this case helped enable >1  $\mu$ s carrier lifetime in low-bandgap tin–lead PSC films.<sup>[10]</sup>

Note that with such additives at lower concentration, long image integration times may be needed. In both images shown in Figure 4, the integration time was more than 1 h to get sufficient signal, which also pushed the SIMS dosage for the image acquisition to about the static SIMS limit of  $1 \times 10^{13}$  ions cm<sup>-2</sup>. When depth profiling is combined with high-resolution imaging, 3D tomography can be realized, which can yield insight into changes of cation gradients and lateral distribution upon changes in processing and/or degradation. Figure 7 shows the 3D tomography renderings for a two-cation perovskite, where one cation is an organic species (shown in red) and the other is inorganic (shown in blue). A gradient in the cations is observed from back to front in all samples. Lateral inhomogeneities between the two cations are

noted at lower processing temperature, and this gradient becomes mostly eliminated at the highest processing temperature.

It is important to note that TOF-SIMS imaging is done using instrument conditions that significantly limit the mass resolution.<sup>[44]</sup> This means that peak overlap and misassignment of peaks are easily possible when using TOF-SIMS imaging; therefore, it is suggested that depth profiling first be performed on a sample under standard profiling conditions where high mass resolution is inherent to the data (surface spectra should be collected at a bare minimum). This will allow the accurate assessment of any possible mass interferences before imaging. The importance of this is illustrated in Figure 8. In recent work it was desired to image sulfur in a perovskite film. Sulfur has two major stable isotopes, <sup>32</sup>S (94.99% abundance) and <sup>34</sup>S (4.25%

abundance). The mass of the main sulfur isotope is 31.9720, while that of an  $O_2^-$  secondary ion cluster falls very nearby at 31.9898. In standard TOF-SIMS profiling conditions the mass resolution is sufficient to separate these two peaks, as shown in Figure 8A. However, when imaging the mass resolution is significantly worse, thus both peaks merge into one centered around mass 32 as shown in Figure 8B, and the imaging information for  $^{32}S^{-}$  cannot be separated from O<sub>2</sub><sup>-</sup>. In such cases, following isotopes of different natural abundance or secondary-ion clusters can sometimes circumvent the issue. While imaging the <sup>34</sup>S<sup>-</sup> peak would be possible, the counts are fairly low leading to significant integration times. One can also consider secondary ion clusters, although care must be taken to ensure the cluster is reflective of the species of interest. In Figure 8C, the <sup>32</sup>S<sup>-</sup>, <sup>34</sup>S<sup>-</sup>, and sulfuriodide (SI<sup>-</sup>) secondary ion cluster profiles are shown, in addition to the iodide profile. One can see that the SI- profile follows the sulfur profiles and not the iodine profile, meaning that peak is reflective of the distribution of sulfur not iodine. This peak has no mass interference issues with



**Figure 7.** TOF-SIMS 3D tomography results for a two-cation perovskite, where one cation is an organic species, and the other is inorganic, processed at different temperatures. Each 3D reconstruction is  $50 \times 50 \times 0.5 \ \mu\text{m}$ . The organic cation is red and inorganic cation is blue. With a lateral resolution of 100 nm or better, TOF-SIMS tomography data such as these can be used to investigate phase segregation and cation distributions in detail through the depth of the film. Reproduced with permission.<sup>[44]</sup> Copyright 2018, American Chemical Society.



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**Figure 8.** A) High mass resolution spectrometry mode spectra showing the 32-sulfur peak, as well as the  $O_2^-$  peak at slightly higher mass. B) Imaging mode spectra showing the same peaks are merged together into one peak centered at mass 32 (blue online), the spectrometry mode peak from A is also shown for comparison (red online). C) Depth profile data showing the  ${}^{32}S^-$ ,  ${}^{34}S^-$ , SI<sup>-</sup> and I<sub>3</sub><sup>-</sup> peaks for a profile, the SI trace is reflective of the sulfur trace and not iodine. The dotted line at 200 nm shows the approximate film/substrate interface.

neighboring peaks and was successfully utilized for imaging and 3D tomography of sulfur. In some cases, high-resolution imaging may not be possible without mass interference issues. Fortunately, many of the typical components of a PSC device do not have serious mass interference issues when imaging; however, as more new passivating additives are being employed, this may not always be the case.

Figure 5A in Section 2.1 shows that the  $Cs_3I_2^+$  and  $Cs_3Br_2^+$  secondary-ion clusters lead to enhanced halide sensitivity when

profiling in positive polarity. However, this methodology does involve a sputtering process that requires both cesium atoms (implanted in the matrix due to the sputter beam) as well as iodine and/or bromine atoms. Thus, it is not intuitively clear if these peaks are used for imaging if the signal measured will be reflective of the spatial distribution of cesium or the halogen ion. To investigate this further, a study was performed where a profile was stopped most of the way through a HTL in a device, so that only part of the underlying PSC film containing



**Figure 9.** TOF-SIMS imaging results showing the utility of the MCs<sup>+</sup> method in imaging the halide ions in positive measurement polarity with increased sensitivity. A profile was stopped in the hole transport layer, where only a small amount of the underlying Br- and I-containing PSC layer was showing. The MCs<sup>+</sup> images were acquired (shown in bottom row), then the instrument polarity was switched to negative to collect the Br- and I- images (shown on top row). In positive polarity, the Br<sup>+</sup> and I<sup>+</sup> images are too low intensity to be above the background level. All the images are 50 × 50  $\mu$ m, and the scale at the right of each image shows the measured intensity in counts per pixel; each image has unique scaling.

iodine and bromine was exposed. The sample was then imaged in positive polarity where the  $Cs_3I_2^+$  and  $Cs_3Br_2^+$  signals were imaged. The measurement polarity was then switched to negative polarity, and the  $Br^-$  and  $I^-$  signals were measured in the same location. The results are shown in **Figure 9**, and one can clearly see from this experiment that the  $Cs_3I_2^+$  and  $Cs_3Br_2^+$  signals have the same spatial distribution as the  $I^-$  and  $Br^-$  signals; this showcases the use of this method for imaging the halide ions in positive polarity, as well.

Surface roughness can influence TOF-SIMS images, because a rough surface (generally >50 nm rms roughness) can change the total ion yield, resulting in apparent image contrast. In newer TOF-SIMS systems from certain manufacturers, data can be collected in a delayed extraction mode that mitigates most of this issue by introducing a slight lag in the time between a primary-ion beam pulse and the field used to extract charged secondary ions into the detector. On systems where delayed extraction is not available, normalizing the images to the total-counts image can help decrease the influence of the surface roughness on the image.<sup>[44]</sup> Detector saturation and mitigation strategies were briefly discussed in Section 2.1 as related to standard profiling. The signal measured in SIMS is directly proportional to the primary-ion beam flux incident on the sample; because the beam flux in imaging mode is generally an order of magnitude or more lower than in high massresolution mode, thus detector saturation is usually not an issue when imaging. However, if it is, then all the mitigation strategies discussed in Section 2.1 still apply.

## 4. Conclusions

TOF-SIMS remains one of the few techniques that can obtain chemical information of all components of halide perovskite photovoltaics, and it can do this in up to three-dimensions with 100 nm or better lateral resolution and sub-nanometer depth resolution. This allows for deep insight into cation distributions (including all organic cations and additives) and how they relate to performance and stability, both within the absorber layer and at interfaces, which is key to advancing the technology. Due to this wealth of useful information provided and the increasing exposure of TOF-SIMS data within the PSC field, it is becoming a more frequently used technique when advanced characterization is needed. Many of the example studies covered here that used TOF-SIMS, sometimes in unique ways, have helped to advance the understanding of PSC materials and devices. As PSC advance toward manufacturing, the examples we discussed regarding the type of data that can be obtained from TOF-SIMS analysis, including depth profiling, high-resolution imaging, and 3D tomography will need to be reapplied in step with changes in PSC processing. The discussed limitations of the technique, with beam damage from the primary-ion beam being of central concern need to be considered but do not undercut the power of the technique. Thus, we showed that beam damage can be mitigated by using a gas cluster ion source combined with the proper measurement conditions when appropriate measurement technique development is undertaken. As the PSC field continues its amazing and rapid-paced march toward more efficient and highly stable devices, TOF SIMS will continue to be an important technique serving a crucial role in providing insight about the distribution and spatial location of many organic components—a benefit that most other advanced characterization techniques cannot provide.

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# **Conflict of Interest**

The authors declare no conflict of interest.

## **Keywords**

degradation, performance, perovskite solar cells, time-of-flight secondary-ion mass spectrometry

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- [1] https://www.nature.com/articles/s41560-018-0323-9.pdf.
- [2] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, J. Am. Chem. Soc. 2009, 131, 6050.
- [3] U.S. Department of Energy, Best Research-Cell Efficiencies, NREL, Golden, CO 2019, https://www.nrel.gov/pv/cell-efficiency.html.
- [4] C. C. Boyd, R. Cheacharoen, T. Leijtens, M. D. McGehee, Chem. Rev. 2019, 119, 3418.
- [5] M. A. Green, A. Ho-Baillie, H. J. Snaith, Nat. Photonics 2014, 8, 506.
- [6] C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith, L. M. Herz, *Adv. Mater.* **2014**, *26*, 1584.
- [7] C. Wehrenfennig, M. Liu, H. J. Snaith, M. B. Johnston, L. M. Herz, Energy Environ. Sci. 2014, 7, 2269.
- [8] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Gratzel, S. Mhaisalkar, T. C. Sum, *Nat. Mater.* 2014, *13*, 476.
- [9] Z. Li, C. Xiao, Y. Yang, S. P. Harvey, D. H. Kim, J. A. Christians, M. Yang, P. Schulz, S. U. Nanayakkara, C.-S. Jiang, J. M. Luther, J. J. Berry, M. C. Beard, M. M. Al-Jassim, K. Zhu, *Energy Environ. Sci.* 2017, 10, 1234.
- [10] J. Tong, Z. Song, D. H. Kim, X. Chen, C. Chen, A. F. Palmstrom, P. F. Ndione, M. O. Reese, S. P. Dunfield, O. G. Reid, J. Liu, F. Zhang, S. P. Harvey, Z. Li, S. T. Christensen, G. Teeter, D. Zhao, M. M. Al-Jassim, M. F. A. M. van Hest, M. C. Beard, S. E. Shaheen, J. J. Berry, Y. Yan, K. Zhu, *Science* **2019**, *364*, 475.

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ENERG

- J. A. Christians, P. Schulz, J. S. Tinkham, T. H. Schloemer, S. P. Harvey, B. J. Tremolet de Villers, A. Sellinger, J. J. Berry, J. M. Luther, *Nat. Energy* 2018, *3*, 68.
- [12] M. Lira-Cantú, Nat. Energy 2017, 2, 17115.
- [13] M. A. Green, A. Ho-Baillie, ACS Energy Lett. 2017, 2, 822.
- N. K. Noel, S. D. Stranks, A. Abate, C. Wehrenfennig, S. Guarnera,
  A.-A. Haghighirad, A. Sadhanala, G. E. Eperon, S. K. Pathak,
  M. B. Johnston, A. Petrozza, L. M. Herz, H. J. Snaith, *Energy Environ. Sci.* 2014, *7*, 3061.
- [15] R. Prasanna, T. Leijtens, S. P. Dunfield, J. A. Raiford, E. J. Wolf, S. A. Swifter, J. Werner, G. E. Eperon, C. de Paula, A. F. Palmstrom, C. C. Boyd, M. F. A. M. van Hest, S. F. Bent, G. Teeter, J. J. Berry, M. D. McGehee, *Nat. Energy* **2019**, *4*, 939.
- [16] T. Zhang, S.-H. Cheung, X. Meng, L. Zhu, Y. Bai, C. Ho, S. Xiao, Q. Xue, S. Kong So, S. Yang, J. Phys. Chem. Lett. 2017, 8, 5069.
- [17] W. Zhang, G. E. Eperon, H. J. Snaith, Nat. Energy 2016, 1, 16048.
- [18] W. C. Lin, H. Y. Chang, K. Abbasi, J. J. Shyue, C. Burda, Adv. Mater. Interfaces 2017, 4, 1600673.
- [19] L. Meng, J. You, Y. Yang, Nat. Commun. 2018, 9, 5265.
- [20] C. Wang, Y. Bai, Q. Guo, C. Zhao, J. Zhang, S. Hu, T. Hayat, A. Alsaedi, Z. a. Tan, *Nanoscale* **2019**, *11*, 4035.
- [21] F. Stevie, Secondary Ion Mass Spectrometry: Applications for Depth Profiling and Surface Characterization, Momentum Press, New York 2015.
- [22] N. Winograd, Anal. Chem. 2005, 77, 142 A.
- [23] S. P. Harvey, F. Zhang, A. Palmstrom, J. M. Luther, K. Zhu, J. J. Berry, ACS Appl. Mater. Interfaces 2019, 11, 30911.
- [24] J. Li, Q. Dong, N. Li, L. Wang, Adv. Energy Mater. 2017, 7.
- [25] T. Zhang, X. Meng, Y. Bai, S. Xiao, C. Hu, Y. Yang, H. Chen, S. Yang, J. Mater. Chem. A 2017, 5, 1103.
- [26] Z. Huang, A. H. Proppe, H. Tan, M. I. Saidaminov, F. Tan, A. Mei, C. S. Tan, M. Wei, Y. Hou, H. Han, S. O. Kelley, E. H. Sargent, ACS *Energy Lett.* **2019**, *4*, 1521.
- [27] K. Domanski, J.-P. Correa-Baena, N. Mine, M. K. Nazeeruddin, A. Abate, M. Saliba, W. Tress, A. Hagfeldt, M. Grätzel, ACS Nano 2016, 10, 6306.
- [28] M. V. Lee, S. R. Raga, Y. Kato, M. R. Leyden, L. K. Ono, S. Wang, Y. Qi, J. Mater. Res. 2017, 32, 45.
- [29] A. F. Akbulatov, L. A. Frolova, M. P. Griffin, I. R. Gearba, A. Dolocan, D. A. Vanden Bout, S. Tsarev, E. A. Katz, A. F. Shestakov, K. J. Stevenson, P. A. Troshin, *Adv. Energy Mater.* 2017, *7*, 1700476.
- [30] F. Matteocci, Y. Busby, J.-J. Pireaux, G. Divitini, S. Cacovich, C. Ducati, A. Di Carlo, ACS Appl. Mater. Interfaces 2015, 7, 26176.
- [31] K. Liang, D. B. Mitzi, M. T. Prikas, Chem. Mater. 1998, 10, 403.
- [32] A. G. Boldyreva, A. F. Akbulatov, M. Elnaggar, S. Y. Luchkin, A. V. Danilov, I. S. Zhidkov, O. R. Yamilova, Y. S. Fedotov, S. I. Bredikhin, E. Z. Kurmaev, K. J. Stevenson, P. A. Troshin, *Sustainable Energy Fuels* **2019**, *3*, 2705.
- [33] Y. Busby, A. Agresti, S. Pescetelli, A. Di Carlo, C. Noel, J.-J. Pireaux, L. Houssiau, Mater. Today Energy 2018, 9, 1.
- [34] M. Ralaiarisoa, Y. Busby, J. Frisch, I. Salzmann, J.-J. Pireaux, N. Koch, Phys. Chem. Chem. Phys. 2017, 19, 828.
- [35] E. M. Sanehira, A. R. Marshall, J. A. Christians, S. P. Harvey, P. N. Ciesielski, L. M. Wheeler, P. Schulz, L. Y. Lin, M. C. Beard, J. M. Luther, *Sci. Adv.* 2017, *3*, eaao4204.
- [36] L. M. Wheeler, E. M. Sanehira, A. R. Marshall, P. Schulz, M. Suri, N. C. Anderson, J. A. Christians, D. Nordlund, D. Sokaras, T. Kroll, S. P. Harvey, J. J. Berry, L. Y. Lin, J. M. Luther, J. Am. Chem. Soc. 2018, 140, 10504.
- [37] Q. Zhao, A. Hazarika, X. Chen, S. P. Harvey, B. W. Larson, G. R. Teeter, J. Liu, T. Song, C. Xiao, L. Shaw, M. Zhang, G. Li, M. C. Beard, J. M. Luther, *Nat. Commun.* **2019**, *10*, 2842.

- [38] Z. Y. Wang, B. W. Liu, E. W. Zhao, K. Jin, Y. G. Du, J. J. Neeway, J. V. Ryan, D. H. Hu, K. H. L. Zhang, M. N. Hong, S. Le Guernic, S. Thevuthasan, F. Y. Wang, Z. H. Zhu, J. Am. Soc. Mass Spectrom. 2015, 26, 1283.
- [39] J. Brison, S. Muramoto, D. G. Castner, J. Phys. Chem. C 2010, 114, 5565.
- [40] C. M. Mahoney, Mass Spectrom. Rev. 2010, 29, 247.
- [41] M. Chen, M.-G. Ju, H. F. Garces, A. D. Carl, L. K. Ono, Z. Hawash, Y. Zhang, T. Shen, Y. Qi, R. L. Grimm, D. Pacifici, X. C. Zeng, Y. Zhou, N. P. Padture, *Nat. Commun.* **2019**, *10*, 16.
- [42] H. Li, L. Tao, F. Huang, Q. Sun, X. Zhao, J. Han, Y. Shen, M. Wang, ACS Appl. Mater. Interfaces 2017, 9, 38967.
- [43] G. Niu, W. Li, F. Meng, L. Wang, H. Dong, Y. Qiu, J. Mater. Chem. A 2014, 2, 705.
- [44] S. P. Harvey, Z. Li, J. A. Christians, K. Zhu, J. M. Luther, J. J. Berry, ACS Appl. Mater. Interfaces 2018, 10, 28541.
- [45] N. Wehbe, J.-J. Pireaux, L. Houssiau, J. Phys. Chem. C 2014, 118, 26613.
- [46] D. Xu, X. Hua, L. Xu, W. J. Wu, Y. T. Long, H. Tian, ACS Appl. Energy Mater. 2019, 2, 2387.
- [47] C. Noël, S. Pescetelli, A. Agresti, A. Franquet, V. Spampinato, A. Felten, A. di Carlo, L. Houssiau, Y. Busby, *Materials* **2019**, *12*, 726.
- [48] C. Noël, Y. Busby, N. Mine, L. Houssiau, J. Am. Soc. Mass Spectrom. 2019, 30, 1537.
- [49] D. Xu, X. Hua, S.-C. Liu, H.-W. Qiao, H.-G. Yang, Y.-T. Long, H. Tian, *Chem. Commun.* 2018, 54, 5434.
- [50] Y. Zhou, X. Yin, Q. Luo, X. Zhao, D. Zhou, J. Han, F. Hao, M. Tai, J. Li, P. Liu, K. Jiang, H. Lin, ACS Appl. Mater. Interfaces 2018, 10, 31384.
- [51] K.-L. Wang, R. Wang, Z.-K. Wang, M. Li, Y. Zhang, H. Ma, L.-S. Liao, Y. Yang, Nano Lett. 2019, 19, 5176.
- [52] D. Wei, F. Ma, R. Wang, S. Dou, P. Cui, H. Huang, J. Ji, E. Jia, X. Jia, S. Sajid, A. M. Elseman, L. Chu, Y. Li, B. Jiang, J. Qiao, Y. Yuan, M. Li, Adv. Mater. 2018, 30, 1707583.
- [53] J. Xue, R. Wang, K.-L. Wang, Z.-K. Wang, I. Yavuz, Y. Wang, Y. Yang, X. Gao, T. Huang, S. Nuryyeva, J.-W. Lee, Y. Duan, L.-S. Liao, R. Kaner, Y. Yang, J. Am. Chem. Soc. 2019, 141, 13948.
- [54] D. H. Kim, C. P. Muzzillo, J. Tong, A. F. Palmstrom, B. W. Larson, C. Choi, S. P. Harvey, S. Glynn, J. B. Whitaker, F. Zhang, Z. Li, H. Lu, M. F. A. M. van Hest, J. J. Berry, L. M. Mansfield, Y. Huang, Y. Yan, K. Zhu, *Joule* **2019**, *3*, 1734.
- [55] M. N. Drozdov, P. A. Yunin, V. V. Travkin, A. I. Koptyaev, G. L. Pakhomov, Adv. Mater. Interfaces 2019, 6, 1900364.
- [56] L. T. Schelhas, Z. Li, J. A. Christians, A. Goyal, P. Kairys, S. P. Harvey, D. H. Kim, K. H. Stone, J. M. Luther, K. Zhu, V. Stevanovic, J. J. Berry, *Energy Environ. Sci.* **2019**, *12*, 1341.
- [57] E. M. Tennyson, B. Roose, J. L. Garrett, C. Gong, J. N. Munday, A. Abate, M. S. Leite, ACS Nano 2019, 13, 1538.
- [58] P. Schulz, D. Cahen, A. Kahn, Chem. Rev. 2019, 119, 3349.
- [59] V. Travkin, G. Pakhomov, P. Yunin, M. Drozdov, Acta Phys. Pol. A 2019, 135, 1039.
- [60] T. D. Siegler, Y. Zhang, A. Dolocan, L. C. Reimnitz, A. Torabi, M. K. Abney, J. Choi, G. Cossio, D. W. Houck, E. T. Yu, X. Li, T. B. Harvey, D. J. Milliron, B. A. Korgel, ACS Appl. Energy Mater. 2019, 2, 6087.
- [61] P. Zhao, B. J. Kim, H. S. Jung, Mater. Today Energy 2018, 7, 267.
- [62] B. Chen, P. N. Rudd, S. Yang, Y. Yuan, J. Huang, Chem. Soc. Rev. 2019, 48, 3842.
- [63] F. Zhang, K. Zhu, Adv. Energy Mater. 0, 1902579.
- [64] J. Kim, A. Ho-Baillie, S. Huang, Sol. RRL 2019, 3, 1800302.