Barrier Design to Prevent Metal-Induced Degradation and Improve Thermal Stability in Perovskite Solar Cells

Caleb C. Boyd,† Rongrong Cheacharoen,† Kevin A. Bush,‡ Rohit Prasanna,§ Tomas Leijtens,¶ and Michael D. McGehee*†‡¶

†Materials Science and Engineering, Stanford University, Stanford, California 94305, United States
‡Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309, United States

Supporting Information

ABSTRACT: Metal-contact-induced degradation and escape of volatile species from perovskite solar cells necessitate excellent diffusion barrier layers. We show that metal-induced degradation limits thermal stability in several perovskite chemistries with Au, Cu, and Ag gridlines even when the metal is separated from the perovskite by a layer of indium tin oxide (ITO). Channels in a sputtered ITO layer that align with perovskite grain boundaries are pathways for metal and halide diffusion into or out of the perovskite. Planarizing the perovskite morphology with a spin-cast organic charge-transport layer results in a subsequently deposited ITO layer that is uniform and impermeable. We show that it is critical to seal the edges of the active layers to prevent escape of volatile species. We demonstrate 1000 h thermal stability at 85 °C in CH$_3$NH$_3$PbI$_3$ solar cells with complete-coverage silver contacts. Our barrier layer design enables long-term thermal stability of perovskite solar cells, a critical step to commercialization.

Perovskite solar cells (PSCs) have the potential to combine high efficiencies with cost-efficient manufacturing techniques for terawatt energy production, especially when used in low-cost tandem solar cells.1–9 However, to realize the benefits of easy-to-manufacture, solution-processable PSCs, their stability must be improved to enable at least a 20–30 year lifetime.10 One of the most important obstacles is metal-contact-induced degradation due to the ubiquitous reactivity of metals and halides and the desire to make the entire electrode out of metal or metal gridlines to reduce series resistance. Although some metals may be stable with respect to the perovskite structure,11 almost all metal species, even platinum, are energetically disposed to form halides.12 Thus, metal contacts act as sinks for halide or halogen species that escape from the perovskite under the stressors of moisture, oxygen, light, and heat, causing irreversible degradation of both the metal contacts and the perovskite active layer.13–23 Gold has also been shown to diffuse through an organic transport layer into the perovskite layer, setting up a two-fold degradation mechanism in which halogen/halide species can diffuse up to the metal and the metal can diffuse into the perovskite (Figure 1A).24 Nonmetal contact layers such as carbon electrodes have enabled excellent PSC stability, but they limit solar cell performance by increasing series resistance losses.25 Transparent conducting oxide (TCO) electrodes such as ITO are often used in single-junction thin-film modules and perovskite tandem solar cells not only because it is necessary for the electrode that is deposited on top of the perovskite to be transparent but also to improve stability.26–28 However, ITO has 2 orders of magnitude higher resistivity than silver27 and can only be used to carry current for approximately 1 cm without causing the series resistance to be unacceptably high.28 There is considerable interest in coating 6 in. wide silicon solar cells with a perovskite cell to make a tandem. Such a cell must have metal gridlines on top of the TCO.

To improve PSC stability while maintaining performance, conductive barrier layers must be developed that prevent both metal and halide species from diffusing in or out of the perovskite active layer. Potential barrier layers include nanostructured carbon layers,26 cross-linked charge-transport layers,30 copper phthalocyanine (CuPC),31 chromium oxide/metal bilayers,32 molybdenum oxide/aluminum bilayers,33–35 aluminum zinc oxide/tin oxide bilayers,36–39 tantalum-doped tungsten oxide/conjugated polymer bilayers,40 and TCOs such as ITO.26 Designing a barrier that can be broadly applied to multiple PSC architectures, prevents decomposition of the perovskite layer, and allows for metal contacts while...
demonstrating impressive thermal stability has proven to be a challenge for the community.

**Au, Cu, and Ag Contacts Degrade PSCs.**

In the first stage of this study, we fabricated PSCs on glass that are identical to those used in world record perovskite−silicon tandem cells previously reported. They had an “inverted” p−i−n architecture ITO/NiOx/FA0.83Cs0.17Pb(I0.83Br0.17)3/evaporated C60/SnO2/ITO/Ag (details in the Experimental Methods) section with semitransparent ITO contacts. We chose this perovskite composition because the use of formamidinium (FA, CH2(NH2)2) and Cs at the A site in ABX3 is known to improve thermal stability.41−43 For this study, we added metal fingers on top of these cells to reduce the series resistance (Figure 1). We found that the introduction of the metal fingers substantially accelerated thermal degradation at 85 °C, a common temperature for accelerated testing of solar cells. We visually saw degradation of the perovskite active layer emanating from Au, Cu, or Ag fingers deposited on the ITO contacts, corresponding to changes in the JV curves of the aged cells and overall PCE loss (Figures 1B,C, S1, and S2 and Table S1). Identical cells without the metal gridlines showed no visible signs of degradation and little to no change in their current−voltage characteristics (Figure S1). We found similar results when we aged MAPbI3 and FA0.75Cs0.25Sn0.5Pb0.5I3 devices with metal gridlines (Figure S1 and Tables S2 and S3). It is very clear that the metal accelerates the degradation because we observed many times that devices made with three different perovskite compositions were much more stable without metal gridlines on top of the ITO, and we could easily see the perovskite film turn yellow near the gridlines.

Because it is not surprising that a reaction between a metal and perovskites would be undesirable, we will not attempt to explain in this Letter precisely what reaction took place between the metals and the perovskites or why the JV curves changed in the way they did. We speculate that metal diffusion into the perovskite layer may react with the perovskite at grain boundaries, creating an insulating layer that leads to decreases in JSC and slight increases in VOC via passivation. We leave this to future work and focus here on demonstrating a highly effective solution for improving the barrier properties of the TCO to prevent the reaction between perovskites and the metal that is needed to reduce series resistance.

**Ag Diffuses through the ITO Layer into the Perovskite Layer and Volatile Halide Species Penetrate the ITO and React with Ag.**

We were surprised by the persistence of metal-induced degradation through both an 8 nm thick atomic-layer-deposited (ALD) SnO2 layer and a 150 nm thick sputtered ITO layer. To confirm that degradation shown in the previous section was due to metal−perovskite reactions, we performed a series of experiments using X-ray photoelectron spectroscopy (XPS) to characterize diffusion of Ag and halide species in and out of the perovskite active layer.

Cells aged at 85 °C in a dark, nitrogen environment for 1000 h with Ag contacts were depth profiled to determine whether Ag diffused into the perovskite layer or not. We used tape to peel off the SnO2, ITO, and metal contacts before depth profiling down into the perovskite layer to avoid diffusion of...
Figure 2. Ag diffuses through the ITO layer into the perovskite layer and volatile halide species penetrate the ITO and react with Ag. (A,C) XPS depth profile to detect Ag present in the perovskite. Tape was used to peel away the top layers of the stack to avoid diffusion of metal into the active layer during sputtering and thus false positives. (C) Ag 3d5 counts measured in the XPS depth profile shown in (A) through two MAPbI₃ PSCs after peeling off the top SnO₂/ITO/Ag layers, one kept at 85 °C and one kept at room temperature for 1000 h in a dark N₂ environment. (B,D) XPS with in situ heating to look for halide diffusion to the metal electrode. (D) XPS spectra on the surface of Ag contacts on MAPbI₃ solar cells heated in situ at 150 °C with evaporated PCBM, an ALD SnO₂ layer, and sputtered ITO covering the surface of the perovskite, showing an increase in iodine species at the surface of the solar cell over the course of 4 h. See also Figures S3–S5.

Figure 3. Planarizing the PSC prevents Ag diffusion. (A,B) Cross-sectional SEM images of ITO barrier layers on MAPbI₃ cells with evaporated (A) and spun (B) PCBM, with red arrows showing diffusion channels in evaporated PCBM that propagate along the rough perovskite grain boundaries. These channels are not present in the layer on spun PCBM. (C,D) Top-down SEM of ITO on MAPbI₃ with evaporated (C) and spun PCBM (D). The channels in the ITO layer match grain boundaries of the perovskite layer. The spun layer effectively smooths the rough perovskite morphology. See also Figures S6–S10.
metal into the active layer during sputtering (Figure 2A). We confirmed that the peel method delaminates the solar cell in the C60 or PCBM layer through XPS, as previously reported.\(^{44}\)

We positively identified Ag peaks in the perovskite active layers of FA\(_{0.83}\)Cs\(_{0.17}\)Pb(\(_{0.83}\)Br\(_{0.17}\))\(_3\), MAPbI\(_3\), and FA\(_{0.75}\)Cs\(_{0.25}\)Sn\(_{0.5}\)Pb\(_{0.5}\)I\(_3\) cells that exhibited degradation after aging at 85 °C (Figures 2B and S3–S5). We used secondary ion mass spectroscopy (SIMS) with depth profiling to further confirm the presence of Ag in the perovskite layer after heating and validate the use of XPS depth profiling to assess the presence of silver (Figure S3). We note that it is difficult to say with certainty where in the perovskite layer the Ag lies due to convoluting effects of roughness during ion milling, ion knock on, and the fact that the grains in the MAPbI\(_3\) do not all traverse through the entire film. However, we did not detect Ag with XPS in the perovskite in fresh cells of any architecture studied in this Letter, in cells that were kept at room temperature for 1000 h, or in cells that were heated for 1000 h without Ag contacts (Figures 2B, S4, and S5). We can therefore strongly conclude that Ag did penetrate the perovskite film aged for 1000 h at 85 °C and that the Ag signal observed by XPS is not an experimental artifact.

While metal diffusion into the active layer is one source of potential degradation, iodide/iodine species escaping the perovskite active layer under both heat and light\(^{15,22,23}\) We performed in situ heating at 150 °C on fresh MAPbI\(_3\) solar cells with evaporated PCBM, ALD SnO\(_2\), and sputtered ITO layers with opaque silver contacts (complete active area coverage) in an XPS tool, taking high-sensitivity scans on the metal contact surfaces over the course of 4 h to look for diffusion of elements out of the perovskite active layer (Figure 2B,D). We chose MA because it is the most volatile A-site cation used in ABX\(_3\) metal halide perovskites, and we wanted to characterize the worst-case scenario. Iodine (or iodide) presence on the surface of the Ag contacts increased drastically during heating, indicating that iodine or iodide species were diffusing out of the active layer to the silver surface. Thus, not only does Ag diffuse into the active layer, but the Ag contact also acts as a sink for iodine from the perovskite, aiding in decomposition of the active layer. Both of these diffusion processes are clearly harmful for device operation and must be prevented for stable PSCs.

Placing the PSC on an Impermeable ITO Layer. ITO has been shown to effectively prevent metal, oxygen, and water vapor diffusion,\(^{45–48}\) contrary to our evidence of degradation due to metal and iodine/iodide diffusion. Because it is not likely that diffusion is occurring through the ITO bulk, improving the morphology of the ITO to prevent diffusion at grain boundaries or through pin holes is the key to improving thermal stability. We tried replacing ITO with the amorphous TCO indium zinc oxide (IZO), which has no grain boundaries and has been shown to be more mechanically stable and thermally stable than ITO, but found that it did not improve the barrier morphology or resistance to metal-contact-induced degradation (Figures S6 and S7).\(^{27,49,50}\) Using scanning electron microscopy (SEM) and atomic force microscopy (AFM), we saw that the morphology of both TCOs drastically changed with planarization of the perovskite layer through spin-coating of the electron-transport layer (ETL) versus evaporating the ETL (Figures 3A–D, S6, and S8). Evaporation conformally coats the perovskite surface, and the sputtered TCO process cannot fill in the deep perovskite grain boundaries. Instead, the perovskite grain boundaries propagate through the TCO layer as channels, as can be clearly been seen in the cross-sectional and top-down SEM images in Figure 3A–D. We observed this grain boundary propagation even with a 500 nm thick TCO (Figure S9). A spun PCBM layer, in
contrast, fills the valleys of the perovskite grains, allowing for a dense, uniform TCO layer. Not coincidentally, many of the devices in other studies that report good stability under light soaking or heating with metal contacts contain barrier layers deposited on solution-processed transport layers such as nanoparticle layers or hole-transport layers.\textsuperscript{26,29,31,32,35,36,40}

Using the same XPS depth profiling experiment as that in the previous section with silver contacts that completely cover MAPbI\textsubscript{3} devices to examine a device in which metal--perovskite reactions would be most likely to occur, we found that the improved TCO layer morphology successfully blocked silver diffusion into the perovskite layer (Figure S10).

While a spun PCBM layer successfully blocked Ag diffusion into the perovskite layer, in situ XPS heating showed that the iodide/iodine signal increased at the surface for cells with both spun and evaporated PCBM that had ITO only on top of the solar cell (Figures 4A,B and S11). To test the hypothesis that the volatile halide species were able to escape from the uncovered edges of the active layer, we sealed the edges of the active layer with ITO (Figure 4C,D). We observed that the amount of iodide/iodine signal that accumulated during in situ heating decreased drastically for the cell with evaporated PCBM and almost completely disappeared for the cell with spun PCBM (Figures S11 and S12). Thus, in addition to having an impermeable TCO layer on top of the perovskite active layer, it is also necessary to seal the edges of the perovskite layer, especially for perovskite compounds that contain volatile organic species such as MA.

1000 h Thermal Stability of MAPbI\textsubscript{3} Solar Cells with an Impermeable TCO. To test the stability of our improved barrier layer in actual devices with a notoriously volatile perovskite, we fabricated MAPbI\textsubscript{3} solar cells with either spun or evaporated PCBM ETLs. We completely covered the active area of the cell with metal to put the barrier properties of the TCO through the toughest test. We deposited an 8 nm thick ALD SnO\textsubscript{2} layer and a 150 nm thick sputtered ITO layer, making sure to extend the ITO layer over the edges of the perovskite active layer to prevent release of the volatile MA species. We used an evaporated MgF\textsubscript{2} insulating strip between the top and bottom ITO layers on one edge of the solar cell in order to prevent shunting and allow for complete ITO coverage of the active layer (Figure S13). We kept three unencapsulated cells of each type with initial efficiencies of 10.1–13.1% on a hot plate in a N\textsubscript{2} glovebox in the dark for 1000 h at 85 °C.\textsuperscript{51} We note that the ALD process had been optimized for a different perovskite compound that produces record efficiency perovskite/silicon tandem solar cells,\textsuperscript{7} and we used MAPbI\textsubscript{3} as a model case to truly challenge the effectiveness of the designed barrier. It is for this reason that the efficiency of our cells is lower than is frequently observed for MAPbI\textsubscript{3}. We saw that all of the cells with evaporated PCBM experienced degradation due to metal diffusion, but remarkably all of the cells with spun PCBM suffered no loss in efficiency (Figures 4 and S14 and Table S2).

We also heated the four MAPbI\textsubscript{3} architectures shown in Figure 4 at 150 °C in ambient air (25 °C, ~40% RH) for 4 h. These test parameters are relevant for packaging commercial solar modules, which often use a 10–20 min, 150 °C encapsulation step. All architectures showed considerable visual degradation except the one with a spun PCBM layer and ITO on the edges as well as the top of the perovskite active layer, which effectively sealed in volatile components and kept moisture and oxygen out of the cell (Figure S15).

In this Letter, we have shown that if metal is used to reduce the series resistance of the electrodes in PSCs then it is necessary to have a dense, channel-free barrier layer to protect the metal from the perovskite and contain volatile components of the perovskite. If there are channels between grains of the perovskite, then it is necessary to solution-cast a contact material to fill in the channels and disrupt the perovskite morphology before sputtering a TCO electrode that serves the dual purposes of carrying current and acting as a diffusion barrier. It is also critically important to seal the edges of the device. If modules are made with laser scribes between cells, it will be necessary to make sure that metal in the vias is protected from the perovskite. We have shown that solar cells made with even one of the most thermally unstable perovskites can be stable for 1000 h at 85 °C even when Ag, which reacts easily with perovskites, is on top of the TCO. We still recommend, however, using the more thermally stable perovskites, a dense TCO barrier layer, and high-quality packaging to maximize the chances of having nearly 100% of the cells operated outside survive for >25 years.

In this study, the only stressing that we subjected the solar cells to was heat. We suspect, however, that the barrier layers described in this Letter will also improve stability under light because a recent paper shows that light accelerates reactions between perovskites and metal contacts by creating mobile halogen vacancies through a process in which photogenerated holes oxidize halogens, making them smaller and allowing them to become interstitials.\textsuperscript{35} In addition to increasing halogen mobility, the photogenerated vacancies allow any oxygen that might be present to penetrate the film and ultimately react with it.\textsuperscript{14} We therefore predict that properly protecting perovskites with barrier layers will allow them to return to their original state unharmed after photoexcitation and are currently testing this hypothesis.

## EXPERIMENTAL METHODS
See the Supporting Information.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b00926.

Detailed methods, tables showing JV characteristics of the species studied, and figures showing pictures of the perovskite cells with different metals and active layers, external quantum efficiencies, depth profiles, XPS spectra, AFM and SEM images, optical microscope images, and the architectures of the cells (PDF)

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: michael.mcgehee@colorado.edu.*

### ORCID

Caleb C. Boyd: 0000-0001-7408-7901
Kevin A. Bush: 0000-0003-1813-1300
Rohit Prasanna: 0000-0002-9741-2348
Tomas Leijtens: 0000-0001-9313-7281
Michael D. McGehee: 0000-0001-9609-9030
Author Contributions
C.C.B., R.C., and M.D.M. designed the experiments and analyzed the data. C.C.B. and R.C. performed the experiments. K.A.B., R.P., and T.L. provided expertise and feedback. C.C.B. and M.D.M. wrote the paper. All authors discussed the results and commented on the manuscript.

Notes
The authors declare no competing financial interest.

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