Supporting Information

Improved Stability and Efficiency of Perovskite Solar Cells with Submicron Flexible Barrier Films Deposited in Air

Nicholas Rolston¹, Adam D. Printz², Florian Hilt², Michael Q. Hovish², Karsten Brüning³, Christopher J. Tassone³, and Reinhold H. Dauskardt^{2*}

¹Department of Applied Physics, Stanford University, Stanford, CA, USA ²Department of Materials Science and Engineering, Stanford University, Stanford, CA, USA ³SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA

*Corresponding author: Prof. Reinhold H. Dauskardt Department of Materials Science and Engineering Stanford University, Stanford, CA 94305-2205 Phone: +1 650 725 0679 Fax: +1 650 725 4034 e-mail: <u>dauskardt@stanford.edu</u>



Figure S1. SEM micrographs of Si wafers after deposition of barrier films from pure precursors. (a) Barrier films formed from pure HMDSO (OBT_0) cracked and delaminated while (b) deposition from pure TFT (OBT_{100}) resulted in negligible film formation.



Figure S2. Cross-sectional SEM micrographs of barrier films on PTAA/ITO-Glass for OBT_1 , OBT_{25} , and OBT_{50} as well as a substrate with no film.



Figure S3. Film thickness of RSPP barrier films as a function of TFT after 5-20 cycles, showing that increasing TFT concentration decreased the deposition rate.



Figure S4. Transmission spectra of the organosilicate barriers on PTAA/ITO-Glass after 15 deposition cycles for OBT_{10} to OBT_{75} . The background used was an uncoated PTAA/ITO-Glass substrate (control, dotted line).



Figure S5. Transmission spectra for films using PTAA/ITO-Glass as a background. (a) Control, PTAA/ITO-Glass, and (b) OBT₁, (c) OBT₁₀, (d) OBT₂₅, (e) OBT₅₀, and (f) OBT₇₅ with different thicknesses.

Figure S6. The relative atomic concentrations of F, Si, C, and O at the surface of barrier films formed from precursors with different concentrations of TFT as measured by XPS survey scans.

Figure S7. The water contact angle (WCA) of barrier films on PTAA/ITO-Glass for different TFT concentrations and numbers of deposition cycles. OBT₂₅ or lower resulted in rougher films which led to higher WCAs, while OBT₅₀ and higher resulted in smoother, more hydrophilic barriers.

Figure S8. The water contact angle (WCA) of barrier films on Si for different TFT concentrations at 15 deposition cycles. As the percent of TFT in the precursor solution increased, the films became more hydrophobic. Inset: Photograph of a water droplet on a OBT_{50} barrier film with a water contact angle of 142°.

Figure S9. J-V curves for a device both before and after barrier film deposition by RSPP, showing an increase in efficiency.

Figure S10. The effect of plasma on the conductivity of the HTL. (a) Setup of the plasma treatment used for exposing PTAA and cross-linked PTAA (PTAAX) films and (b) sheet resistance measured with a four-point probe of films after various cycles, showing an immediate decrease in sheet resistance from plasma exposure.

Figure S11. XPS survey scans of PTAA films (a) as prepared, (b) after one cycle, and (c) after five cycles of plasma exposure, simulating the conditions experienced during barrier film deposition.

Figure S12. Atomic concentrations of the elements contained within PTAA as a function of exposure cycles to the plasma, showing a clear increase in oxygen content from the plasma.

Comparison of RSPP barrier films to evaporated and sputtered SiO₂

We documented an observed increase in PCE in perovskite solar cells with RSPP barrier films. To observe if this improvement was limited to the spray-plasma deposition method, 100

nm films of pure silica were also deposited by e-beam evaporation and magnetron sputtering in order to observe any changes in device performance. The devices with evaporated barrier films remained in an inert environment under high vacuum for the entire deposition, conditions which would not further oxidize the PTAA film. The resulting PCE decreased slightly due to decreased J_{sc} (**Figure S13**), which is potentially from the high temperature process (SiO₂ has a melting point of over 1,700 °C) thermally degrading the perovskite into PbI₂.

The devices with sputtered barrier films were exposed to an O_2 plasma during deposition and experienced an increase in PCE similar to that observed in the devices with spray-plasma deposited barriers. The primary conclusion is that at temperatures below the volatilization temperature for the perovskite cation, plasma exposure enhanced the performance of LiTFSIdoped devices.

Figure S13. J-V curves for a device both before and after SiO_2 barrier film deposition by evaporation and sputtering, showing a decrease in efficiency after evaporation and an increase in efficiency after sputtering, suggesting that the plasma enhances device efficiency.

Figure S14. The normalized PCE for the best-performing barrier protected device compared to an unprotected control aged in damp heat for 150 h.

Figure S15. Photographs of barrier-protected and uncoated perovskite solar cells submerged in water. The barrierprotected perovskite remained intact after 15 min, while the uncoated perovskite degraded to PbI_2 .

Figure S16. 2D XRD scans of perovskite samples before heating (a) without a barrier film (control), (b) OBT_{25} , and (c) OBT_{50} .

Figure S17. Normalized peak area vs time extracted by integrating the 2D XRD scan over the PbI_2 peak (yellow) and the MAPbI₃ (100) peak (black) of perovskite samples while heating at 180 °C (a) without a barrier film (control), (b) OBT₂₅, and (c) OBT₅₀.

Figure S18. X-ray Photoelectron Spectroscopy depth profiles showing the elemental composition in the barrier, PTAA, and perovskite layers for (a) an unaged control, (b) a control aged at 180 °C for 1 h, and (c) an OBT₂₅ coated sample aged at 180 °C for 1 h.

Figure S19. Micrographs of methylammonium (MA) egress from OBT_{50} and unprotected (control) perovskite solar cells on a hotplate (85 °C) in ambient air under illumination (4230 W m⁻²). The control perovskite device turns yellow around 37.5 min, while the encapsulated device shows no signs of yellowing.

Figure S20. MA egress from OBT_{50} and unprotected (control) perovskite solar cells on a hotplate (85 °C) in ambient air under illumination (microscope light). (a) MA egress was tracked by mass spectrometry (m/z=31) and a noticeable peak occurred for the control device. Inset, left: Photographs showing yellowing of the perovskite (conversion to PbI₂ due to MA egress) at the point of illumination for the unprotected perovskite, while the OBT_{50} device remained unchanged. Inset, right: An expansion of the MA egress peak in the mass spectrometry scan. (b) A photograph of the OBT₅₀ device after 40 h of exposure to light, heat, and moisture, showing no evidence of perovskite yellowing.

Figure S21. Gas phase mass spectrometry for MAPbI₃ on glass to track MA egress (m/z=31) at a temperature a) ramped from 25°C to 180 °C over 5 min and b) held at 250 °C, showing a noticeable peak which increases in sharpness with temperature.

Figure S22. AFM images (10 x 10 μ m) of as-received polyimide substrate and PTAA-coated polyimide, showing a locally smooth morphology amenable for the deposition of barrier films on these flexible substrates.

Figure S23. a) Photograph of the mechanical bending test showing a barrier film at a 1 cm bending radius and b) displacement vs. time showing 10 bending cycles of the sample.

Figure S24. G_c of the barrier film as a function of TFT concentration, showing that TFT incorporation is necessary for improved adhesion.