

Power Conversion Efficiency Enhancement of Low-Bandgap Mixed Pb—Sn Perovskite Solar Cells by Improved Interfacial Charge Transfer

Tingming Jiang,[†] Zeng Chen,[‡] Xu Chen,[†] Xinya Chen,[†] Xuehui Xu,[†] Tianyu Liu,[†] Lizhong Bai,[†] Dexin Yang,[†] Dawei Di,[†] Wei E. I. Sha,[⊥][®] Haiming Zhu,[‡][®] and Yang Michael Yang^{*,†}[®]

[†]State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310058, China

[‡]Center for Chemistry of High-Performance & Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310058 China

¹Key Laboratory of Micro-nano Electronic Devices and Smart Systems of Zhejiang Province, College of Information Science and Electronic Engineering, Zhejiang University, Hangzhou 310027, China

Supporting Information

ABSTRACT: The power conversion efficiency (PCE) of low-bandgap mixed Pb-Sn perovskite solar cells (PSCs) has been significantly hindered by large open-circuit voltage (V_{oc}) loss and poor fill factor (FF). Herein, mixed Pb–Sn perovskite films with a composition $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ were processed with a simple delayed annealing (DA) treatment that enables perovskite films with significantly reduced surface roughness. The treatment reduces nonradiative recombination of interfacial contacts when the perovskite films are interfaced with poly(3,4ethylenedioxythiphene):poly(styrenesulfonate) (PEDOT:PSS) and fullerene (C_{60}) . Charge transfer at the carrier-collection interfaces has been effectively improved, in agreement with time-resolved photoluminescence (TRPL) and transient photovoltage/photocurrent results. Consequently, the champion cell based on perovskite films with DA treatment shows a high $V_{\rm oc}$ of 0.824 V, indicating a greatly suppressed $V_{\rm oc}$ loss (for a bandgap of ~1.25 eV), and an overall PCE of over 18.6%.



rganic-inorganic metal halide perovskite solar cells (PSCs) have achieved tremendous progress in the past few years due to their high optical absorption coefficients, high charge carrier mobility, long charge carrier diffusion, low exciton binding energy, bandgap tunability, and low-temperature solution processability.¹⁻⁸ The power conversion efficiency (PCE) of single-junction perovskite cells has been boosted from 3.8%9 in 2009 to a recent record of 23.3%.10,11

Despite the rapid revolution of the record PCEs for singlejunction PSCs, the ultimate PCE of single-junction PSCs is governed by the Shockey–Queisser (SQ) limit.¹² According to the SQ theory, the inefficiency in converting above- and belowbandgap photons is a dominant loss for a solar cell. The most reliable strategy for improving the PCEs to beyond the SQ limit of single-junction photovoltaics is to establish tandem cell structures.¹³⁻¹⁶ Currently, the wide-bandgap PSCs used as a top subcell generally employ Pb-based mixed halide perovskite with a tunable bandgap from 1.6 to 2.5 eV by varying the ratio of I and Br.17-19 Meanwhile, the mixed Pb-Sn iodide

perovskite is usually utilized as the absorbers for low-bandgap bottom subcells with a tunable bandgap from 1.6 to 1.2 eV.^{16,20-25} So far, the development of efficient wide-bandgap PSCs has been successful, while the progress of low-bandgap mixed Pb–Sn is considered slow, primarily due to the large open-circuit voltage $(V_{\rm oc})$ loss^{26–28} and the diffucultly in fabricating thick, uniform mixed Pb-Sn perovskite films. Therefore, the development of high-performance low-bandgap mixed Pb-Sn PSCs is an important subject of research.

It is encouraging that the low-bandgap Pb-Sn mixed PSCs have shown prosperous progress in the last 2 years especially considering the much improved PCEs. The groups of Kanatzidis and Jen have independently reported low-bandgap $MASn_xPb_{1-x}I_3$ PSCs with the PCE over 10% for the first time.^{29,30} In 2016, Yan and co-workers reported a mixed Pb-Sn PSCs with a high PCE to 15% by using a blending

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Figure 1. (a) Schematic illustration of $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ perovskite film preparation. (b) XRD patterns and fits from Rietveld refinements of perovskite films without and with DA treatment. (c) Absorption spectra of perovskite films without and with DA. (d,e) Topview SEM images of perovskite films without and with DA. (f,g) AFM topography images of perovskite films without and with DA (scan size: $4 \mu m \times 4 \mu m$).

precursor solution.³¹ Later, they further improved the PCE up to $17.6\%^{23}$ by increasing the $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ film thickness to extend the carrier lifetime. In 2018, Hayase and co-workers achieved a PCE of 17.6% for low-bandgap PSCs by building a conduction band spike structure between the perovskite and the electron-transport layer.²⁷ Xu et al. achieved a high PCE of over 18% by inserting an ultrathin organic semiconductor layer between the perovskite and PEDOT:PSS, effectively suppressing the open-circuit voltage loss.²⁶ Recently, the Yan group continued to optimize (FASnI₃)_{0.6}(MAPbI₃)_{0.4} low-bandgap PSCs with the highest PCE over 19% via Br incorporation, which reduced the saturation current.²⁰ Just upon completion of this paper, Yan and Zhu et al. achieved PCEs of over 20% for mixed Pb-Sn low-bandgap PSCs via the addition of guanidinium thiocyanate (GuaSCN), substantially reducing the defect density in perovskite films.³

However, the difficulties in growing thick, uniform, and high-quality Pb–Sn perovskite films to generate high photocurrent and engineer energy band alignment to suppress the $V_{\rm oc}$ loss have been the primary factors restricting the further improvement of PCE for low-bandgap mixed Pb-Sn PSCs. In this work, we managed to significantly enhance the $V_{\rm oc}$ by improving the interfacial charge transfer and charge extraction between perovskite films and charge-transport layers via a simple annealing treatment to modify the mixed Pb-Sn perovskite film morphologies. We have developed a simple delayed annealing (DA) process to control the crystal growth of thick (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskite films with the thickness of ~580 nm by controlling the solvent evaporation rate. It is reported that DMSO with a high boiling point could not easily escape from the film after antisolvent rinsing. The residual DMSO solvent is able to enhance the mass transport and diffusion, improving the film quality with slower evaporation rate.³³ On the basis of this strategy, upon the formation of a perovskite film after spin-coating, the films were first kept in a dry N₂-filled glovebox for about 15 min and then were annealed under 100 °C for 10 min. The surface roughness of the perovskite films processed by this treatment has been significantly reduced compared to the films annealed immediately. The PSCs adopting $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$



Figure 2. (a) Steady-state PL spectra of $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ perovskite films without and with DA. (b) Plots of absorption as a function of photon energy to extract Urbach energies for perovskite films with and without DA. Normalized TRPL decay profiles of the $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ perovskite films grown on bare glass (c), on PEDOT:PSS (d), and capped with 25 nm C₆₀ (e).

perovskite films with DA as absorbers show a champion PCE of 18.6% with an insignificant hysteresis, while the best cell with films annealed immediately have the highest PCE of 14.17%. The $V_{\rm oc}$ and fill factor (FF) were improved from 0.747 V and 67.4% to 0.824 V and 75.4%, respectively. We consider that the reduced surface roughness of the films by DA have increased the contact area with the charge-transport layers (PEDOT:PSS and C₆₀). This leads to improved collections of carriers at the charge-transport interfaces, contributing to the PCE enhancement of the devices.

We prepared $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ perovskite films through the spin-coating method by mixing precursor solution FASnI₃ and MAPbI₃ in a ratio of 6:4. For simplicity, we label the films annealed immediately after spin-coating as "W/O DA", whereas the films processed with DA are denoted as "With DA". The process of film fabrication is sketched in Figure 1a. The crystallization of (FASnI₃)_{0.6}(MAPbI₃)_{0.4} films grown on PEDOT:PSS with and without DA has been evaluated by X-ray diffraction (XRD) measurement, as shown in Figure 1b as well as with calculated XRD patterns. According to a previous report,³¹ (FASnI₃)_{0.6}(MAPbI₃)_{0.4} mixed Pb-Sn perovskites adopt an orthorhombic crystal structure with space group Amm2. The calculated XRD patterns agree well with the experimental data, and two intense and sharp (011) and (022) diffraction peaks indicate highly orientated crystal growth. Values of lattice parameters for perovskite films with DA are a = 6.3027 Å, b = 8.9466 Å, c= 8.8979 Å, and V = 501.73 Å³, while for films without DA, the values are a = 6.3025 Å, b = 8.9461 Å, c = 8.8979 Å, and V =501.65 Å³. No evident changes are observed for the lattice parameters, implying that the DA treatment has not caused any change to the crystallization of the perovskite phase. The

optical absorption spectra of the perovskite films are plotted in Figure 1c, in which one can observe that the absorption edge of the perovskite film with DA treatment has a slight blue shift of about 10 nm compared to the films without DA. The estimated optical bandgaps are about 1.25 and 1.24 eV for the two films.

Figure 1d,e shows the top-view SEM images of (FASnI₃)_{0.6}(MAPbI₃)_{0.4} films spin-coated on an ITO/PEDOT:PSS substrate with and without DA treatment. The films for the two cases are both compact, uniform, and pinhole-free, exhibiting similar average grain sizes of 400-500 nm, which are highly desirable for fabricating efficient PSCs. However, compared to the films without the DA treatment (Figure 1d), the films with the DA treatment appear to be much smoother (Figure 1e). SEM images with higher magnification are shown in Figure S1. In order to investigate the morphological difference in greater detail, we carried out atomic force microscopy (AFM) measurements, as shown in Figure 1f,g. The root-mean-square roughness of the films without DA (Figure 1f) is determined to be 35.1 nm, which is considerably larger than 19.8 nm for the films with DA (Figure 1g), indicating that the DA process has substantially reduced the surface roughness of the perovskite films.

We further carried out steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements for perovskite films grown on bare glass, PEDOT:PSS substrates, and perovskite films capped with 25 nm C_{60} to investigate the effect of charge carrier extraction. One can observe from Figure 2a that the PL spectra of films with and without DA show similar spectral shape except for a slight 10 nm blue shift in emission peak for films with DA treatment compared to that of films without DA. This emission peak shift



Figure 3. (a) Schematic of the device architecture of inverted PSCs. (b) J-V curves of PSCs without and with DA under 100 mW cm⁻² AM 1.5G illumination under reverse and forward scans. (c) EQE spectra (left axis) and integrated J_{sc} (right axis) of PSCs without and with DA. (d) Histogram of PCEs measured for 35 cells.

is in agreement with the observation in optical absorption spectra shown in Figure 1c. To evaluate the electronic quality of the mixed Pb-Sn perovskite films treated with and without DA, we calculated the Urbach energies by combing emission and absorption spectra shown in Figure 2b. The Urbach energies of the films with and without DA treatment are 14.7 and 14.5 meV. The difference of 0.2 meV is within the error range of our estimation. These Urbach energies of the films are smaller than those of the previous report,²³ suggesting that the perovskite films that we prepared have a lower density of trap states. The perovskite films prepared using the two methods possess similar Urbach energies, implying that they have similar optically active defect densities. This indicates that the DA treatment has limited influence on the optoelectronic properties of the films. Figure 2c shows the PL decay spectra of perovskite films with and without DA on bare glass, in which both can be fitted by single exponential functions with PL lifetimes on the order of 100 ns. This indicates that the perovskite films that we prepared have reasonably good electronic quality required for photovoltaic operation, in agreement with the small Urbach energies calculated. The photogenerated carrier lifetimes have been determined to be 117 and 115 ns for films with and without DA. The very similar PL lifetimes indicate that the DA treatment has no observable influence on the electronic properties of the films. This is also in line with the similar Urbach energies calculated for these films. These results point to suppressed nonradiative recombination, enabling good $V_{\rm oc}$ and FF for solar cells. To investigate the charge-transfer effect, TRPL measurements

were performed on perovskite films prepared on PEDOT:PSS (Figure 2d) and perovskite films covered with 25 nm C_{60} (Figure 2e) with and without the DA treatment. The PL decay spectra of perovskite films on PEDOT:PSS (Figure 2d) can be fitted by a biexponential decay function: $i = A_1 \exp(-t/\tau_1) +$ $A_2 \exp(-t/\tau_2)$, with fast and slow decay lifetimes of τ_1 and τ_2 and prefactors of A_1 and A_2 .³⁴ Because the perovskite film is interfaced with the hole-transport layer PEDOT:PSS, the PL decay process consists of a carrier recombination process in the bulk region, as characterized by the slow decay lifetime τ_{2i} as well as a charge-transfer process at the interface, as characterized by the fast lifetime τ_1 .³⁵ For perovskite films with the DA treatment, the fast decay lifetime τ_1 and its percentage weighting A_1 in the whole decay process are calculated to be 4.58 ns and 45.9%, while for films without DA treatment the corresponding values are 4.74 ns and 32.9%. All of the fitting parameters are listed in Table S1. This comparison suggests that the hole transfer from the perovskite layer to PEDOT:PSS is more efficient for films with DA treatment, consistent with shorter decay lifetime τ_1 and a higher A_1 value compared to those of films without DA treatment.

PL decay spectra of perovskite films capped with 25 nm C_{60} with and without DA treatment shown in Figure 2e show a trend similar to the case of perovskite films grown on the PEDOT:PSS hole-transport layer. The fast decay lifetime τ_1 and its percentage A_1 have been estimated to be 0.44 ns and 76.0% for perovskite films with the DA treatment, while they are 0.48 ns and 73.1% for films without DA. These results are



Figure 4. Modeled and experimental J-V characteristics of PSCs without and with DA.

Table 1. Retrieved Characteristic Parameters from Measured J-V Curves of PSCs without and with DA and Simulated $V_{oct} J_{sc}$, and FF

	γ	R _s	$R_{ m sh}$	$J_{\rm sc}$	$V_{\rm oc}$	FF	PCE
condition	$[10^7 S^{1-}]$	$[10^{-4} \text{ Ohm } m^2]$	[Ohm m ²]	$[mA cm^{-2}]$	[V]	[%]	[%]
W/O DA	635	0.8	0.0537	28.76	0.748	69.9	15.04
With DA	154	0.37	240	29.99	0.825	76.4	18.86

consistent with the view that the electron extraction is also more efficient for the case of perovskite films treated with DA than the films without DA. All of the fitting parameters are placed in Table S1. The improved charge transfer between the perovskite layer and PEDOT:PSS and C₆₀ for the perovskite films treated with DA can be attributed to the increased interfacial contact area due to the reduced roughness of perovskite films enabled by the DA process. In addition, the PL spectra of perovskite films grown on bare glass, PEDOT:PSS, and films capped with 25 nm C_{60} are shown in Figure S2. For both films with and without DA, significant PL quenching can be observed by comparing the spectra intensity of perovskite films on bare glass and perovskite films interfaced with PEDOT:PSS and C₆₀. However, the PL quenching for films with DA is more intense than that for films without DA, consistent with possible improvements in interfacial charge carrier extraction.

We fabricated the solar cell devices adopting the inverted pi-n architecture shown in Figure 3a, which consists of glass/ ITO/PEDOT:PSS/(FASnI₃)_{0.6}(MAPbI₃)_{0.4}/ C_{60} /BCP/Ag. Figure 3b shows the current density-voltage (J-V) curves of the devices using $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ perovskite films with and without DA treatment in both forward and reverse scan directions. The highest PCE of device-based perovskite films without DA is 14.47% with a $V_{\rm oc}$ of 0.747 V, $J_{\rm sc}$ of 28.75 mA/ cm², and FF of 67.4%, while for the best-performing device with a DA-treated perovskite film, the V_{oc} and FF significantly improved to 0.824 V and 75.7%, respectively, while the J_{sc} slightly increased to 29.95 mA/cm², resulting in an enhanced PCE of 18.6%. The significant enhancement in $V_{\rm oc}$ and FF for devices with DA-treated perovskite films can be ascribed to the improved interfacial charge transfer between the perovskite layer and C₆₀, PEDOT:PSS charge extraction layers. The external quantum efficiencies of the solar cells have also been investigated, as shown in Figure 3c. The two spectra both demonstrate a broad spectral response extending to 1050 nm, in line with the optical absorption results. It is noteworthy to mention that for perovskite cells with the DA treatment the EQEs in the near-infrared wavelength range of 700-850 nm

are over 70%, which is an important spectral region for the bottom cell in a perovskite tandem device. However, the spectrum in the range of 820-1050 nm for the perovskite films without DA has a lower spectra response compared to that of films with DA, resulting in a slightly lower integrated J_{sc} . The integrated J_{sc} values from the EQE spectra for perovskite films with and without DA treatment are 28.27 and 27.56 mA/cm^2 , respectively, which are slightly lower than those obtained from the J-V characteristics. This difference could be possibly due to the lower illumination intensity of the EQE light source. However, the deviation is less than 6%, which is still reasonable, as discussed by Zimmermann et al.³⁶ Figure 3d displays the histogram of the PCE values of 35 devices for a perovskite film with DA, suggesting that nearly 85% of the devices were able to exhibit PCEs of over 16.8%. Meanwhile, as shown in Figure S3, the maximum steady-state PCEs of the device with DA show a stable PCE of 18.2%, which is slightly lower than the value (18.6%) obtained from the J-V curve of the forward scan. For the device with the highest PCE, it has been stored in an N₂-filled glovebox without encapsulation for 30 days. The remeasured PCE is 17.6%, retaining over 92% of the initial efficiency. This suggests that the mixed Pb-Sn perovskite is reasonably stable over time (Figure S4).

We further used a modified detailed balance model to understand the loss mechanism and quantify the energy losses in our low-bandgap PSCs. This model is governed by the formula below

$$J = \frac{V - JR_{s}}{R_{sh}} + J_{n}(V - JR_{s}) + J_{r}(V - JR_{s}) - J_{p}$$

in which V is the applied voltage of a solar cell. $J_{\rm p}$ is the photocurrent. $J_{\rm r}$ and $J_{\rm n}$ are the current losses resulting from radiative and nonradiative recombination. More details about the formula and physical meanings can be found elsewhere.³⁷ Given a J-V curve, the curve can be modeled to retrieve three primary parameters, including the nonradiative recombination rate γ , the series resistance $R_{\rm s}$, and the shunt resistance $R_{\rm sh}$. $R_{\rm s}$ is related to the ohmic loss at the contact, carrier-transport layers, as well as heterojunction interfaces between the



Figure 5. Normalized TPC (a) and TPV (b) for PSCs without and with DA.

perovskite and carrier-transport layers. R_{sh} is an indication of the defects and pinhole-induced current leakage. Figure 4 shows the modeled and experimentally measured J-V curves of PSCs with and without DA treatment. Table 1 shows the retrieved characteristic parameters from measured J-V curves. It can be seen that the three quantities γ , R_{s} , and R_{sh} for the device with DA treatment are 1.54×10^9 s⁻¹, 3.7×10^{-5} Ohm· m², and 240 Ohm·m², respectively, much improved compared to those of the device without the DA treatment. It is worth pointing out that the nonradiative recombination rate γ for the device with DA is 4 times lower than that of the device without DA. It is generally considered that the nonradiative recombination is related to the perovskite crystal quality. On the basis of the SEM, XRD, and TRPL analyses above, the perovskites with and without DA treatment both show good signs of crystallization, exhibiting large grain sizes and long photocarrier lifetimes on glass, despite the difference in surface roughness. Therefore, the noticeable decrease in γ suggests a significantly reduced surface recombination at the perovskitecharge-transport layer interfaces. Meanwhile, the reduced R_s with the DA treatment agrees with the increased interfacial contact area. In addition, current leakage related to high interfacial roughness can be reduced by the DA treatment, as characterized by the increased $R_{\rm sh}$.

We also explored the transient photocurrent (TPC) decay under the short-circuit condition and transient photovoltage (TPV) decay under the open-circuit condition, shown in Figure 5. The charge-transport time for PSCs with DA treatment is estimated to be 551 ns, shorter than the value (719 ns) for cells without DA, in agreement with faster charge transport. In the meanwhile, the charge recombination lifetime for devices with DA treatment is about 14.4 ms, which is substantially longer than 9.9 ms for the devices without DA. Under the open-circuit condition upon illumination, electrons and holes are generated and recombine within the active layer without flowing to the external circuit. When the illumination stops, the separated holes and electrons undergo recombination in the dark, resulting in photovoltage decay. From the TRPL and Urbach energy analysis that we discussed earlier, we have confirmed that the perovskite films with and without DA have a similar optoelectronic quality and bulk PL lifetimes; therefore, the prolonged charge recombination lifetime from TPV decay for the device with DA can be explained by slower interfacial charge recombination, possibly related to the reason that faster carrier extraction prevents charge accumulation at the perovskite-charge extraction layer interfaces. The TPV

and TPC results may be used to further understand the improved interfacial charge transfer and more efficient charge extraction between the perovskite films and the PEDOT:PSS and C_{60} layers due to the improved interfacial contact for the devices with DA treatment.

In summary, the low-bandgap $(FASnI_3)_{0.6}(MAPbI_3)_{0.4}$ mixed Pb-Sn perovskite films prepared by DA treatment exhibit a much lower surface roughness compared to that of perovskite films with an immediate annealing process, as confirmed by the SEM and AFM comparisons. The perovskite films with much smoother surface morphology show more efficient hole and electron extraction when interfaced with PEDOT:PSS and C₆₀, consistent with our TRPL analysis and TPV and TPC measurements. This can be attributed to the increased contact area between the perovskite layer and the charge-transport layers. The improved interfacial charge transfer leads to overall device performance enhancement for the best solar cell showing a $V_{\rm oc}$ of 0.824 V, $J_{\rm sc}$ of 29.95 mA/ cm², and FF of 75.4% compared to a V_{oc} of 0.747 V, J_{sc} of 28.75 mA/cm^2 , and FF of 67.4% for the best device without DA treatment. Our findings demonstrate that a simple DA treatment to the perovskite films can give rise to substantial device performance improvement for the low-bandgap mixed tin-lead PSCs, highlighting that perovskite film processing still remains to be an important issue in the development of PSCs.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.9b00880.

Experimental details, computational details, supporting analysis of SEM, PL, and TRPL parameters of the mixed Pb–Sn perovskite films, photocurrent output and efficiencies of the champion cell at the maximum power point, and the device stability test (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail:yangyang15@zju.edu.cn.

ORCID 💿

Wei E. I. Sha: 0000-0002-7431-8121 Haiming Zhu: 0000-0001-7747-9054 Yang Michael Yang: 0000-0002-3362-7155

Notes

The authors declare no competing financial interest.

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Letter