Efficient tandem solar cells with solution-processed perovskite on textured crystalline silicon

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resulting in 400- to 600-nm-thick films), pyramids that were not capped with perovskite were observed, and these regions created shunt paths in devices (fig. S1). To fully cover the micrometer-sized pyramids, we used a concentrated (1.65 to 1.75 M) precursor that resulted in a micrometer-thick perovskite with large (2 to 4 μm) grain sizes (Fig. 1B). This process enabled us to achieve uniform perovskite coverage of the pyramids and eliminated the need for additional flattening processes (Fig. 1, C and D).

To achieve current matching, we opted to broaden the band gap of the micrometer-thick perovskite rather than reduce the thickness of a smaller band gap perovskite because the latter approach would uncover pyramids. This thick, wide-band gap perovskite (1.68 eV, Cs0.05MA0.15FA0.8PbI2.25Br0.75) top cell also provided a path toward a higher ultimate efficiency limit in tandem solar cells (fig. S2).

Because the size of the Si pyramids and perovskite thickness were similar, this infiltrated morphology differs from previously reported flat and conformal architectures used in perovskite-silicon tandem devices (fig. S3) (7, 8, 14, 15). These images also suggest that the textured structures substantially modified the surface geometry by increasing the contact area. Rather than producing a conformal coating with uniform thickness, which would be similar to the evaporation case, the solution-processed perovskite smoothly overcoated the pyramid geometry while retaining the curvature of the textured surface beneath (Fig. 1D). The elemental distribution within the tandems measured by means of energy-dispersive x-ray spectroscopy (EDS; Fig. 1E) confirmed the presence of a textured layer stack. From the detailed features of the perovskite and conformal NiOx interface, we did not see undesired accumulation of hole-transport layer (HTL) material at the bottom, nor did we observe HTL material absence at the facets of the Si pyramids (7, 8, 14, 15).

Thick perovskite layers require sufficiently long charge-carrier diffusion lengths to enable efficient charge collection. This condition demands perovskite crystals and surfaces of high electronic quality. To increase the performance of single-junction wide-band gap PSCs, much research has focused on developing surface treatments (22). Trioctylphosphine oxide (TOPO) can substantially reduce radiative recombination and increase perovskite stability (23), but its insulating nature inhibits charge transport in devices. In addition, the rough surface of textured c-Si devices sets an additional challenge in the search for surface passivation. A passivant film must conformally coat and passivate the rough top perovskite surface with readily controlled thickness and functional groups without being overly sensitive to surface topography, treatment time, and perovskite thickness. Moreover, this treatment should not dissolve the perovskite nor alter its crystal structure (24).

We pursued an approach in which we exposed the rough perovskite top surface to 1-butanethiol vapor, a technique adapted in light of previous work performed on thiol-based self-assembled monolayer growth on metal surfaces. The thiol group anchored to the perovskite surface by strong coordination of the thiol on Pb2+. The thiol molecules rapidly...
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**Fig. 2.** Effects of SLP on diffusion length and phase segregation in micrometer-thick wide-band gap perovskite. (A) TRPL spectra of 1.68-eV-band gap thin films under different surface treatments. a.u., arbitrary units. (B) Normalized PL spectra of control perovskite films after illuminating for 0, 10, and 20 min. (C) Normalized PL spectra of SLP-treated perovskite films after illuminating for 0, 10, and 20 min. (D) Nanoscale-resolved mapping of the area indicated by the light blue square in (E) (100 nm by 100 nm) of the diffusion length of the control perovskite. The white dashed line shows the corresponding grain-boundary (GB) area. (E) Contact-mode atomic force microscopy (AFM) topography of the control sample (top) and SLP perovskite (bottom) (scale bar, 100 nm). (F) Nanoscale-resolved mapping of the area indicated by the dark blue square in (E) (100 nm by 100 nm) of the diffusion length of the SLP perovskite. The white dashed line shows the corresponding GB area.

**Diffused through the vapor phase to the perovskite surface, in contrast with thiol passivation of PbS colloidal quantum dots, where ligand exchange occurred in solution. Because of the self-limiting nature of thiol passivation, no anchoring sites were present after the initial passivation for further growth of additional layers. Thus, prolonged exposure did not damage the perovskite.

We used ultrafast transient absorption spectroscopy to investigate the phase distribution of 1.68-eV-band gap perovskite films after different treatment times. The two classes of treated films each showed a single ground-state bleaching peak centered at ~725 nm (fig. S4). This result indicated that the perovskite films existed compositionally within a single phase and that the bulk properties of the perovskite film could be stabilized with the thiol self-limiting passivation (SLP) treatment. We confirmed identical recombination kinetics for the film after 30-min and 20-hour SLP treatments: The data (fig. S4) attest to the time-insensitivity of the passivation process. Similarly, there were no differences in surface-sensitive grazing-incidence wide-angle x-ray scattering (GIWAXS) measurements between the samples with different SLP treatment times. After different treatment times, the perovskite peaks maintained their intensities and positions, suggesting no change in crystal structure and orientation (fig. S5).

After SLP treatment, we observed in time-resolved photoluminescence (TRPL) an increase in the carrier lifetime from 570 to 900 ns when we measured the samples from air-perovskite sides. This is ~15% higher than that of similar films treated with TOPO (Fig. 2A) and ~60% higher than that of control samples. We propose that passivation using smaller-sized thiols provided increased diffusion through the vapor phase and reduced steric hindrance. When we illuminated from the glass-perovskite side, the carrier lifetime was essentially similar in these three samples (fig. S6). Passivation was most effective on the top surface of thick perovskite, where, in the pristine case, major carrier recombination would otherwise have occurred.

The SLP treatment also enhanced phase stability of the perovskite. After 20 min of continuous light exposure, the SLP-treated films exhibited a stable PL peak position, whereas the control sample showed a red shift in the peak position, indicative of phase segregation (Fig. 2, B and C). This result is in agreement with earlier conclusions from Belisle et al. demonstrating that charge accumulation and carrier trapping at perovskite surfaces are drivers of photoinduced halide segregation and that efficiently passivating the perovskite surfaces suppresses phase segregation and stabilizes wide-band gap perovskites (25).

A representative, randomly selected 100-nm–by–100-nm area for topographic imaging that included grain boundaries (red square in fig. S7) was mapped for the nanoscale charge-carrier diffusion length, which is related to the local charge-carrier transport time (fig. S8) and charge-carrier recombination lifetime (fig. S9). Figure 2, D to F, presents nanoscale diffusion-length maps of both control sample and SLP-treated perovskite at similar regions, indicated by the blue squares. The diffusion length was improved in both grain and grain boundaries for SLP perovskites compared with control samples. The diffusion length in SLP perovskites within grains was ~570 nm. At the grain boundaries, the diffusion length of the SLP perovskite decreased by ~50 nm, whereas the diffusion length in the control sample decreased by ~100 nm (fig. S10). Thus,
passivation of the grain boundaries for the SLP perovskite increased the charge diffusion length compared with the control sample.

To probe the effects of the textured structure on the electrical field in the vertical direction, we used nanometer-scale KPFM to profile and observe the differences in electric-potential (or electric-field) distribution across the flat and textured devices. To determine the bulk profile from the surface measurement, we applied different forward-bias voltages of 1 and 1.5 V to the device and imaged the cross-sectional surface potential under each voltage (figs. S11 to S20). The junction characteristic was assessed from the small current flow, or equivalent shunt resistance, under bias, which was acquired by measuring the voltage drop across the cross-sectional surface.

By taking the first derivative of the potential difference, we determined the electric-field distribution relative to the metallurgical interfaces (Fig. 3, A to I). We observed two prominent junction peaks at the HTL-perovskite and perovskite–electron-transport layer (ETL) interfaces, whereas the electric field was near zero inside the perovskite layer. The perovskite-ETL junction has a similar strength and depletion width for both flat and textured cells, which agreed with the perovskite-ETL interfaces being identical for these two devices. Interestingly, the electric field at the HTL-perovskite interface was enhanced when a textured substrate was used (Fig. 3, J and K).

We determined that the depletion region in the perovskite (at the HTL-perovskite interface) was much wider at the valley of Si pyramids (~380 nm) than at their top (~120 nm) or compared with flat perovskite cells. This result implies that where the perovskite was the thickest, the depletion width was the largest, which would be desirable for effective charge collection. At the pyramid valleys, the perovskite was more confined and was subjected to electrical fields superimposed from neighboring HTL-coated pyramids. When Si
The EQE-integrated perovskite cells as a function of perovskite layer thickness. The red dot represents the EQE-integrated J SC value on the textured tandem top cell. (B) Calculated J SC values of the perovskite cells as a function of perovskite layer thickness. The red dot represents the EQE-integrated J SC value in the textured tandem top cell. (C) Measured weighted reflectance as a function of pyramid sizes of c-Si. Texturing size refers to the pyramid base. The SEM images of different texturing sizes are reported in the insets (scale bar, 2 μm). (D) J–V characteristics of flat, textured, and SLP-treated textured tandems. (E) J–V characteristics of certified SLP-treated textured tandems. (F) MPP tracking of certified SLP-treated textured tandems and PCE distributions of 88 individual tandem devices. (G and H) EQE of the flat (G) and textured (H) devices (integrated current of 18.2 mA/cm² for the top cell and 16.8 mA/cm² for the bottom cell in the flat device; 19.3 mA/cm² for the top cell and 19.2 mA/cm² for the bottom cell in the Fraunhofer ISE CalLab PV Cells–certified textured device). (I) J–V curves of tandem devices before encapsulation (glass and butyl rubber) at the beginning and the end of the 85°C stability test. (J) J–V parameters measured over a 400-hour stability test at 85°C (relative humidity ~45 to 50%). (K) J–V curves of the tandem devices before encapsulation (glass and POE) at the beginning and the end of the MPP stability tests. (L) J–V parameters measured over ~400 hours of light-soaking under MPP load at 40°C.

Pyramid valleys were sharper, depletion regions were wider (in a linear relation; detailed values are shown in tables S1 and S2), which further suggested that the depletion width correlates with the geometry factor. In contrast with the case of other deposition methods (such as coevaporation), this geometry was only observed when the solution-processed perovskite cells smoothed out the textured silicon cell and caused this beneficial geometry-dependent electric-field distribution. This finding agrees with the simulated results (fig. S21).

The KPFM observation accounted for device performance trends, in that charge collection increases with layer thickness. The red dot represents the EQE-integrated J SC value of the ~1.1-μm-thick perovskite used in this work (fig. S22), which is within ~10% of the theoretical limit. This certified ~19.3 mA/cm² J SC value is among the highest values for a single-pass device with 1.68-eV–band gap perovskites (fig. 4H). In contrast with opaque devices with reflection from the rear electrode, single-junction devices required a thicker absorber to capture more photons near the band edge. With more photons absorbed by the top cell, we expect an enhanced upper limit of tandem efficiency.

Spectrally weighted reflectances were calculated from the air mass (AM) 1.5 G spectrum in the range of 350 to 900 nm (fig. 4C). To investigate the effect of pyramid size on the reflection loss, we also selected different Si pyramid sizes by tailoring the texturing process. Although the pyramids in commercial Si are typically in the range of 2 to 7 μm, the benefit to reflection began to saturate when the pyramid size reached 2 μm or less (see fig. S23). This result is encouraging for perovskite-silicon tandems because it suggests that well-established solution-processing techniques can be united with textured silicon (fig. S24).

We observed enhanced J SC and FF in tandems (fig. 4D and figs. S24 and S25) in the case of fully textured c-Si bottom cells. EQE measurements highlight the advantage of switching from a polished front side to a double-side textured architecture (fig. 4, G and H). Reflections occurring in the flat design...
induced more current loss in the 330- to 1200-nm range. The introduction of a front texture reduced the overall reflectance, especially at wavelengths of 550 and 800 nm. The $J_{SC}$ integrated from the EQE spectra is in excellent agreement with that derived from the 1-sun current—voltage ($J-V$) curve with enhanced $J_{SC}$ in both the top cell and bottom cell on the double-side textured device.

Both differential EQE and absorption confirm the ~1.68-eV perovskite band gap (fig. S2). We observed narrower EQE overlap between the perovskite and Si cell. The textured-device EQE maintained a plateau at 92 to 93% in this region. This result is distinct from previous work based on 400- to 600-nm-thick perovskite on flat devices in which the perovskite lost EQE at wavelengths of 550 and 800 nm. This high EQE photocurrent, combined with enhanced charge extraction, resulted in high FF, leading to an improved device performance from 20.3 to 24.0% (table S3). In particular, by further adding SLP treatment, we observed a distinct increase of FF from 72 to 77% (Fig. 4D). By reducing the recombination area and improving the top contact design (fig. S26), we achieved a Fraunhofer ISE CalLab PV Cells-certified stabilized (at MPP) PCE of 25.7% (Fig. 4, E and F, and fig. S27).

The tandems reported herein show low hysteresis (Fig. 4E), high reproducibility (Fig. 4F and fig. S28), and excellent operational stability under accelerated tests (Fig. 4, I to L). We monitored the stability of devices encapsulated with glass and butyl rubber. We heated these devices to 85°C for 400 hours in the dark at ~40% relative humidity and found that the devices retained their original performance (Fig. 4, I and J). We also monitored 400-hour operating stability of devices encapsulated using glass and POE (polyolefin encapsulant): Here, we used 1-sun-equivalent illumination (fig. S29) at 40°C and ~40 to 50% relative humidity (Fig. 4, K and L). $J-V$ curves in both scan directions [open-circuit voltage ($V_{OC}$) to $J_{SC}$ and $J_{SC}$ to $V_{OC}$] were measured at 10-min intervals at 100 mV/s from ~0.1 to +1.9 V, and vice versa. Between measurements, the tandem solar cell was held at the MPP voltage as determined by the most recent $J-V$ scan. Devices retained their original performance after 400 hours. In Fig. 4, I to K, the $J-V$ curves of the tandem were reported before encapsulation, at the beginning of the test, and after 400 hours, and images are provided of devices at the end of the test. Overall, we attribute this good operating lifetime to the replacement of organic-carrier-selective layers with NiO$_x$ inorganic materials, which prevent iodine reaction with small-molecule organic HTLs (table S4).

REFERENCES AND NOTES


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SUPPLEMENTARY MATERIALS

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Efficient tandem solar cells with solution-processed perovskite on textured crystalline silicon


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Growing perovskite on textured silicon

Wide-band gap perovskites could boost the efficiency of silicon solar cells by forming tandem cells, but usually the perovskite must be grown on a smoothed side of the silicon cell because the material grown on the rough light-trapping side often does not fully coat the silicon surface and its rough texture is prone to phase separation. Hou et al. grew thick films of a perovskite with a band gap of ~1.68 electron volts and used a passivant, 1-butanethiol, to limit its phase separation. The tandem cells had a certified power conversion efficiency of 25.7% and had negligible losses after 400 hours of operation.

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