PRECURSOR SOLUTIONS FOR PEROVSKITE SOLAR CELLS

FIELD OF THE INVENTION

This invention is in the field of perovskite solar cells and for methods involving precursor solutions for making the same.

BACKGROUND

Solar cells, also referred to as photovoltaic cells, are optoelectronic devices that convert light into electricity using the photovoltaic effect. Silicon solar cells are capable of converting light within a wavelength range of about 300 nanometers ("nm") to 1100 nm into electricity. However, the conversion efficiency of silicon solar cells decreases appreciably as the wavelength of light decreases from 1100 nm. Additionally, silicon solar cells are unable to convert wavelengths of light above about 1100 nm to electricity because such photons lack the energy required to overcome the band gap of silicon.

A tandem solar cell has two individual solar cells stacked on top of one another, where a top cell absorbs incident light, and a bottom cell absorbs residual light transmitted through the top cell. The bottom cell can be a silicon solar cell, and the top cell can be composed of a different material. The top cell can have a higher band gap than the silicon solar cell. Accordingly, the top cell can be capable of efficiently converting shorter wavelengths of light to electricity. The top cell can be transparent to longer wavelengths of light, which can allow the underlying silicon solar cell to absorb and convert such longer wavelengths of light to electricity. Thus, the tandem solar cell can generate electricity over a wider wavelength range of light and with a higher conversion efficiency than either cell individually. Generally, a solar module (also referred to as a solar panel) is composed of multiple solar cells electrically connected in series, parallel, or series/parallel. A solar module can also include other components, such as a frame, a junction box, etc.

Perovskite solar cells generally include a layer of a perovskite material. Such layers can be formed by coating a solution containing a precursor onto a substrate and treating the precursor to form the perovskite material.

SUMMARY

The present disclosure describes manufacturing methods for making perovskite solar cells using solvent coating methods.

Coating perovskite films through solution processes commonly utilizes polar solvents with high boiling points and low vapor pressures at room temperature, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and n-methyl-2-pyrrolidinone (NMP). These solvents have relatively slow evaporation rates, which hinder supersaturation, thereby limiting nucleation and growth rates. While perovskite solar cells hold promise for next-generation energy production due to their high power conversion efficiency (PCE), the efficiency of large-area modules still trails behind small-area cells. Conventional methods for generating crystal nuclei in perovskite thin films involves increasing solute supersaturation through rapid extraction of high-boiling point solvents using antisolvents during the spin-coating process. This process cannot easily be scaled up and extended to large-area fabrication techniques such as blade-coating and/or slot-die process.

Therefore, for effective large-area coating, selecting a co-solvent with a low boiling point and high vapor pressure can be used to beneficially influence the solvent evaporation rate. This can balance fast nucleation and slowed crystal growth, resulting in uniform and dense perovskite films. Suitable co-solvent candidates include tetrahydrofuran (THF) and acetonitrile (ACN). THF, for example, has a relatively high vapor pressure (127 mmHg at 20°C) and low boiling point (66°C) with low toxicity. Furthermore, THF can enhance the hydrophilicity and wetting behavior of solutions, which can aid in producing pinhole-free films with excellent coverage. Such properties are considered important for coating of large area samples.

In this approach, one scenario involves preparing the initial stock solution with a higher molarity (concentration) compared to the typical daily concentration, and then using THF to dilute it to the desired end concentration. This process yields a perovskite film with increased thickness and a compact morphology. Another option is to dilute the original stock solution with the target concentration further, without compensating for thickness. This approach can lead to reduced material consumption while still achieving the desired film morphology and uniformity.

In general, the solution coating techniques described here can be used for forming a variety of solar modules that incorporate perovskite solar cells, including single perovskite

solar modules and tandem solar modules, e.g., with a tandem silicon-perovskite solar cell. A tandem silicon-perovskite solar module as described herein is a solar module composed of two solar modules stacked on each other. The solar modules include a silicon solar cell and a perovskite solar cell, with the perovskite solar cell usually stacked on top of the silicon solar cell. That is, when installed, sunlight is first incident on the perovskite solar cell. The perovskite solar cell generally has a higher bandgap than the silicon solar cell. For example, the perovskite solar cell can have a bandgap of about 1.7 electron volts ("eV") while the silicon solar cell has a bandgap of about 1.1 eV. Accordingly, the perovskite solar cell is capable of efficiently converting shorter wavelengths of light to electricity. The perovskite solar cell can be transparent to longer wavelengths of light, which allows the underlying silicon solar cell to absorb and convert such longer wavelengths of light to electricity. Together, the perovskite solar cell and the silicon solar cell are capable of efficiently converting a wider spectrum of light to electricity than a single solar cell, e.g., there may be less thermalization loss in a tandem solar module than in a single solar module resulting in a higher full spectrum efficiency. The addition of perovskite solar cells can improve the resultant solar modules by decreasing cost, improving performance per weight of the module, improve overall performance of the module, and the like.

In a tandem module, a silicon solar cell can be a monocrystalline or multi-crystalline silicon solar cell. The silicon solar cell can be a component of a conventional solar panel. The solar panel may have a back sheet on which the silicon solar cell is disposed. An encapsulant can cover the top of the silicon solar cell to prevent it from being exposed to dust and moisture.

The perovskite solar cell can be deposited on a bottom surface of the top glass sheet. This differs from the construction of conventional tandem solar cells in which a perovskite cell is disposed directly on top of a silicon wafer. Depositing the perovskite solar cell on the bottom surface of the top glass sheet allows manufacturers to incorporate perovskite solar cells into their conventional silicon solar panels with no re-tooling or process changes. Instead, manufacturers can merely substitute a conventional glass sheet with the perovskite glass sheet. This disclosure may refer to the perovskite glass sheet, or perovskite-on-glass, as "active glass."

The perovskite solar cell includes a first transparent conducting oxide ("TCO") layer which can be deposited on the top glass sheet, a hole transport layer ("HTL") deposited on the first TCO layer, a perovskite layer deposited on the HTL, an electron transport layer ("ETL") deposited on the perovskite layer, and a second TCO layer deposited on the ETL.

The first and second TCO layers can serve as terminals for the perovskite solar cell. The ETL and HTL facilitate electron and hole transport, respectively, while inhibiting hole and electron transport, respectively. The perovskite layer can absorb light to generate charge carriers, which results in a voltage and current flow across the terminals of the perovskite solar cell.

The perovskite solar cell and the silicon solar cell can be electrically isolated from each other, and each cell can have its own terminals. That is, the tandem solar cell can be a 4-terminal cell. The perovskite solar cell and the silicon solar cell can be connected in series or parallel by connecting the terminals in the appropriate manner. In the case of a series connection, the perovskite solar cell and the silicon solar cell can be current-matched. In the case of a parallel connection, the perovskite solar cell and the silicon solar cell can be voltage- matched.

Other aspects of the present disclosure provide methods of fabricating and manufacturing the devices and components described above and elsewhere in this disclosure.

Additional aspects and advantages of the present disclosure will become readily apparent to those skilled in this art from the following detailed description, where only illustrative embodiments of the present disclosure are shown and described. As will be realized, the present disclosure is capable of other and different embodiments, and its several details are capable of modifications in various obvious respects, all without departing from the disclosure. Accordingly, the drawings and description are to be regarded as illustrative in nature, and not as restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A schematically illustrates an example tandem, 4-terminal, silicon-perovskite solar cell.

FIG. 1B schematically illustrates a perovskite solar cell.

FIG. 2 schematically illustrates a perovskite solar cell having an encapsulant.

FIG. 3 is a flowchart of an example fabrication process for forming a perovskite photovoltaic.

FIG. 4A-4D show steps of an example method for forming a layer of a perovskite material on a substrate.

FIG. 5 is a flowchart of a fabrication process for forming a tandem solar cell.

Like elements in different drawings are identified by like reference numbers.

DETAILED DESCRIPTION

Referring to FIG. 1A, an example tandem, 4-terminal, silicon-perovskite solar cell 100 includes a top glass sheet 105, a perovskite solar cell 240, an encapsulant 135, a silicon solar cell 140, and a back sheet 145.

The top glass sheet 105 protects underlying layers of the solar cell 100 from dust and moisture. The solar cell 100 can be part of a solar module that has a form factor that corresponds to a conventional silicon solar panel. For example, the top glass sheet 105 can have a form factor that corresponds to a 32-cell, 36-cell, 48-cell, 60-cell, 72-cell, 96-cell, or 144-cell silicon solar panel. The top glass sheet 105 can have a thickness of at least about 2.0 millimeters (mm), 2.5 mm, 3.0 mm, 3.5 mm, 4.0 mm, 4.5 mm, 5.0 mm, or more. The top glass sheet 105 can have a thickness of at most about 5.0 mm, 4.5 mm, 4.0 mm, 3.5 mm, 3.0 mm, 2.5 mm, 2.0 mm, or less. The top glass sheet 105 may be transparent to allow light to access the underlying solar cells. In some cases, the top surface of the top glass sheet 105 may be covered with magnesium fluoride (MgF2) and/or polydimethylsiloxane (PDMS) (e.g., 1:10 alumina PDMS, textured 1:50 alumina PDMS, or textured PDMS), which generally improves light trapping and refractive index matching. In some examples, the top surface of the top glass sheet 105 is covered with an anti-reflective coating to reduce reflections of light within a particular spectral range. Alternatively, or in addition, the bottom surface of the top glass sheet 105 can be textured in order to enable more light scattering back into the perovskite solar cell 240.

FIG. 1B schematically illustrates the perovskite solar cell 240 of the solar cell 100 depicted in FIG. 1A. The perovskite solar cell 240 includes a first transparent conducting oxide (TCO) layer 110, a hole transport layer (HTL) 115, a perovskite layer 120, an electron transport layer (ETL) 125, and a second TCO layer 130. The perovskite solar cell 240 can be disposed on the bottom surface of the top glass sheet 105 through fabrication methods that are described in FIGs. 3-7. Further details relating to such manufacturing methods are described in Int'l. Appl. No. PCT/US2021/051465, filed September 22, 2021, and titled Methods and Devices for Integrated Tandem Solar Module Fabrication, which is incorporated herein by reference in its entirety for all purposes.

The perovskite solar cell 240 generally has a higher bandgap than the silicon solar cell 140. For example, the perovskite solar cell 240 can have a bandgap of about 1.30 electron volts ("eV") to 2.10 eV, or greater. The perovskite solar cell 240 may have a bandgap of about 1.30, 1.31, 1.32, 1.33, 1.34, 1.35, 1.36, 1.37, 1.38, 1.39, 1.40, 1.41, 1.42,

1.43, 1.44, 1.45, 1.46, 1.47, 1.48, 1.49, 1.50, 1.51, 1.52, 1.53, 1.54, 1.55, 1.56, 1.57, 1.58, 1.59, 1.60, 1.61, 1.62, 1.63, 1.64, 1.65, 1.66, 1.67, 1.68, 1.69, 1.70, 1.71, 1.72, 1.73, 1.74, 1.75, 1.76, 1.77, 1.78, 1.79, 1.80, 1.81, 1.82, 1.83, 1.84, 1.85, 1.86, 1.87, 1.88, 1.89, 1.90, 1.91, 1.92, 1.93, 1.94, 1.95, 1.96, 1.97, 1.98, 1.99, 2.00, 2.01, 2.02, 2.03, 2.04, 2.05, 2.06, 2.07, 2.08, 2.09, 2.10, or greater eV. In contrast, the silicon solar cell 140 can have a bandgap of about 1.1 eV. Accordingly, the perovskite solar cell 240 is capable of efficiently converting shorter wavelengths of light to electricity compared to the silicon solar cell 140. The perovskite solar cell 240 can be transparent to longer wavelengths of light, which allows the underlying silicon solar cell 140 to absorb and convert such longer wavelengths of light to electricity. Together, the perovskite solar cell 240 and the silicon solar cell 140 can be capable of efficiently converting a wider spectrum of light to electricity than a single solar cell.

The first TCO layer 110 can be disposed directly on the top glass sheet 105. Depositing the first TCO layer 110 directly on the top glass sheet 105 can prevent damage to the HTL 115 and the perovskite layer 120. The first TCO layer 110 can serve as the positive terminal or cathode of the perovskite solar cell 240. The first TCO layer 110 can have a thickness of at least about 100 nanometers (nm), 200 nm, 300 nm, 400 nm, 500 nm, 600 nm, 700 nm, 800 nm, 900 nm, 1 micrometer, or more. The first TCO layer 110 may have a thickness of at most about 1 micrometer, 900 nm, 800 nm, 700 nm, 600 nm, 500 nm, 400 nm, 300 nm, 200 nm, 100 nm, or less. The first TCO layer 110 can be made of indium tin oxide (ITO). The first TCO layer 110 can be made of doped ITO. The TCO layer 110 can have a resistance of at least about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, or more Ohm/square meter. The TCO layer 110 can have a resistance of at most about 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, or less Ohm/square meter.

The HTL 115 is disposed on the first TCO layer 110. The HTL 115 facilitates the transport of holes from the perovskite layer 120 to the first TCO layer 110 without compromising transparency and conductivity. In contrast, the HTL 115 inhibits electron transport. In some embodiments, the HTL 115 is made of one or more nickel oxide layers. In other embodiments, the HTL 115 is made of another appropriate p-type material described in this disclosure. The HTL 115 can have a thickness of at least about 5 nm, 10 nm, 20 nm, 50 nm, 100 nm, 200 nm, 300 nm, 400 nm, 500 nm, 600 nm, 700 nm, 800 nm, 900 nm, 1 micrometer, or more. The HTL 115 may have a thickness of at most about 1 micrometer, 900

nm, 800 nm, 700 nm, 600 nm, 500 nm, 400 nm, 300 nm, 200 nm, 100 nm, 50 nm, 20 nm, 10 nm, 5 nm, or less.

The perovskite layer 120 is disposed on the HTL 115. The perovskite layer 120 is the photoactive layer of the perovskite solar cell 240. That is, the perovskite layer 120 absorbs light and generate holes and electrons that subsequently diffuse into the HTL 115 and the ETL 125, respectively. In some embodiments, the perovskite layer 120 is made of methylammonium lead triiodide, methylammonium lead tribromide, methylammonium lead trichloride, or any combination thereof. In other embodiments, the perovskite layer 120 is made of formamidinium lead triiodide, formamidinium lead tribromide, formamidinium lead trichloride, or any combination thereof. In other embodiments, the perovskite layer 120 is made of cesium lead triiodide, cesium lead tribromide, cesium lead trichloride, or any combination thereof. In some embodiments, the perovskite layer 120 can be a triple cation perovskite material with formamidinium, methylammonium, and cesium cations in different ratios. Incorporating cesium into the perovskite lattice can provide enhanced thermodynamic stability. The bandgap of the perovskite layer 120 can be tuned by adjusting the halide content of the methylammonium lead trihalide or formamidinium lead trihalide. The perovskite layer 120 can have a thickness of at least about 250 nm, 300 nm, 400 nm, 500 nm, 600 nm, 700 nm, 800 nm, 900 nm, 1 micrometer, 1.25 micrometers, 1.5 micrometers, 1.75 micrometers, 2 micrometers, or more. The perovskite layer 120 can have a thickness of at most about 2 micrometers, 1.75 micrometers, 1.5 micrometers, 1.25 micrometers, 1 micrometer, 900 nm, 800 nm, 700 nm, 600 nm, 500 nm, 400 nm, 300 nm, 250 nm, or less.

The ETL 125 is disposed on the perovskite layer 120. The ETL 125 facilitates the transport of electrons from the perovskite layer 120 to the second TCO layer 130 without compromising transparency and conductivity. In contrast, the ETL 125 inhibits electron transport. In some embodiments, the ETL 125 is made of phenyl-C61-butyric acid methyl ester ("PCBM"). In other embodiments, the ETL 125 is made of another appropriate n- type material described in this disclosure (e.g., C60). The ETL 125 can have a thickness of at least about 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm, 90 nm, 100 nm, 200 nm, 300 nm, 400 nm, 500 nm, or more. The ETL 125 can have a thickness of at most about 500 nm, 400 nm, 300 nm, 200 nm, 100 nm, 90 nm, 80 nm, 70 nm, 60 nm, 50 nm, 40 nm, 30 nm, 20 nm, 10 nm, or less. The interface between the ETL 125 and the perovskite layer 120 can be important to the performance of the perovskite layer 120. The surface of the perovskite layer 120 can be hydrophilic to enable good coverage of a hydrophilic ETL (e.g., PCBM). The combination of environment (e.g., low humidity <15%, low temperature from 18 to 24

degrees Celsius) and solvent compatibility can impact the quality of the perovskite layer-ETL connection.

The second TCO layer 130 is disposed on the ETL 125. The second TCO layer 130 can serve as the negative terminal or anode of the perovskite solar cell 240. The second TCO layer 130 can have a thickness of at least about 100 nm, 200 nm, 300 nm, 400 nm, 500 nm, 600 nm, 700 nm, 800 nm, 900 nm, 1 micrometer, or more. The second TCO layer 130 can have a thickness of at most about 1 micrometer, 900 nm, 800 nm, 700 nm, 600 nm, 500 nm, 400 nm, 300 nm, 200 nm, 100 nm, or less. The second TCO layer 130 can be made of indium oxide (ITO). The second TCO layer 130 may be made of doped ITO.

The encapsulant 135 is disposed on the second TCO layer 130. The encapsulant 135 can electrically isolate the perovskite solar cell 240 from the silicon solar cell 140. Moreover, the encapsulant 135 can have a relatively high refractive index (e.g., roughly equal to or greater than 1.4) that matches the refractive index of the top silicon nitride or TCO layer of the silicon solar cell 140. Thus, using a high refractive index material(s) can decrease transmission losses between the second TCO layer 130, encapsulant layer 135, and silicon solar cell 140, resulting in improved current density of the solar cell 100. The use of a high refractive index material(s) can also improve light trapping. For example, the encapsulant 135 can include ethylene-vinyl-acetate ("EVA"), thermal plastic polyolefin ("TPO"), PDMS, silicone, paraffin, or the like. The encapsulant 135 can also isolate both the perovskite solar cell 240 and the silicon solar cell 140 from the surrounding environment. The encapsulant 135 can be configured to prevent volatilization of one or more components of the perovskite layer 120. For example, the encapsulant 135 can minimize loss of organic cations (e.g., methylammonium, formamidinium, etc.) due to heating of the perovskite layer 120. In another example, the encapsulant 135 can reduce the egress of chemical species from the perovskite layer 120 such as lead iodide or other lead halides, the egress of which can result in degraded reliability of the integrated tandem cell 100. The encapsulant 135 can be treated to have sufficient cross linking to protect the perovskite layer 120 from water, oxygen, volatilization of the organic compounds of the perovskite layer 120, or the like, or any combination thereof. The encapsulant 135 can have a cross linked percentage of at least about 50, 60, 70, 80, 90, 95, or more percent. The encapsulant 135 can have a cross linked percentage of at most about 95, 90, 80, 70, 60, 50, or less percent.

In general, the silicon solar cell 140 can be a p-type silicon solar cell with a p-type substrate covered by a thin n-type layer ("emitter"), or it may be an n-type silicon solar cell with an n-type substrate covered by a thin p-type emitter. The silicon solar cell 140 can be a

monocrystalline silicon solar cell, a polycrystalline silicon solar cell, a PERC silicon solar cell, a HIT silicon solar cell, an interdigitated back contact cell (IBC), or the like.

The silicon solar cell 140 can have a back sheet 145. The back sheet 145 seals the solar cell 100 to prevent moisture ingress. In some cases, the back sheet 145 can be a glass sheet with a top surface and a bottom surface. The top surface of the glass sheet may have a highly reflective coating or textured surface to further increase light trapping or scattering back into the silicon solar cell 140 and the perovskite solar cell 240. The glass sheet can be transparent. The glass sheet can be substantially transparent. The transparency of the glass sheet can facilitate bifacial operation of the solar cell 100. For example, the solar cell 100 can be configured to absorb light from both sides of the cell 100.

The perovskite solar cell 240 and the silicon solar cell 140 can be electrically isolated from each other, and each cell may have its own terminals. That is, the tandem solar cell 100 can be a 4-terminal module with each solar cell having two respective terminals. The perovskite solar cell 240 and the silicon solar cell 140 can be connected in series or parallel by connecting the terminals in the appropriate manner. In the case of a series connection, the perovskite solar cell 240 and the silicon solar cell 140 can be current-matched. In the case of a parallel connection, the perovskite solar cell 240 and the silicon solar cell 140 can be voltage matched. Laser scribing can be used to achieve the current matching or voltage matching, e.g., by connecting individually scribed perovskite solar cells in series or parallel to achieve a desired voltage or current. Parallel or series connection between the perovskite solar cell 240 and the silicon solar cell 140 can be made via busbars/electrodes before cell lamination. This allows rapid and easy introduction into any existing silicon manufacturing process.

A solar module containing cell 100 can have a power conversion efficiency of at least about 25%, 26%, 27%, 28%, 29%, 30%, or more.

FIG. 2 schematically illustrates a perovskite solar cell 200 encapsulated with an encapsulant 135 for protecting P1, P2, and P3 scribe lines. The perovskite solar cell 200 is an example of a perovskite solar cell that can be used in isolation or integrated with a silicon solar panel to form a tandem silicon-perovskite solar cell, e.g., the tandem silicon-perovskite solar cell 100 of FIG. 1A.

In more detail, FIG. 2 shows a cross-sectional view of the perovskite solar cell 200. The perovskite solar cell 200 includes a first TCO layer 110, a HTL 115, a perovskite (PVSK) layer 120, an ETL 125, and a second TCO layer 130 that form a perovskite solar cell 240. The solar cell 200 further includes an anode terminal 201 and a cathode terminal 202

that interface with the perovskite solar cell 240, e.g., to output power. For clarity, the HTL 115 and ETL 125 are depicted as solid lines to illustrate the various interconnects between the TCO layers 110 and 130, the perovskite layer 120, and the terminals 201 and 202. The perovskite solar cell 240 is disposed on a glass substrate 105, e.g., a bottom surface of a top glass sheet. The encapsulant 135 is disposed on the perovskite solar cell 240, encapsulating the underlying layers of the solar cell 240. The encapsulant 135 fills the scribe lines P1-P3 and bonds with the terminals 201 and 202. In general, the encapsulant 135 protects the scribe lines P1-P3, provides structural stability, improves electrical isolation, and passivates the exposed surface of the solar cell 240.

Anode region 211 and cathode region 212 designate opposite sides of the solar cell 200 where the two terminals 201 and 202 of the photovoltaic 200 reside. The anode region 211 includes the anode terminal 201 that is electrically connected to the first TCO layer 110. The anode 201 is electrically isolated from the perovskite layer 120 and second TCO layer 130 due to a gap (G1) in these layers that is filled with the encapsulant 135. The cathode region 212 includes the cathode terminal 202 that is electrically connected to the first TCO layer 110 and the second TCO layer 130. The cathode region 212 also includes a number of scribe lines P1-P3 that perform various functions such as forming interconnects. The bulk of the solar cell 200 resides in the space between the two regions 211 and 212 which can include multiple individually scribed perovskite segments. In particular, each individually scribed perovskite segment can be separated by a corresponding set of scribe lines P1-P3 to form serial interconnections (e.g., monolith interconnections) between the perovskite segments.

Scribe lines P1-P3 correspond to respective gaps in one or more layers of the solar cell 200 that allow overlapping layers to be deposited into the gaps to form contacts. For example, P1 scribe corresponds to a gap in the first TCO layer 110 that is filled by the PVSK layer 120, the second TCO layer 130, and the encapsulant 135. The P1 scribe isolates the first TCO layer 110 between neighboring perovskite segments. The P2 scribe corresponds to a gap in the PVSK layer 120 that is filled with the second TCO layer 130 and the encapsulant 135. The P2 scribe provides a channel to connect the first TCO layer 110 of one perovskite segment to the second TCO layer 130 of the next perovskite segment to form an interconnection. The P3 scribe corresponds to a gap in the PVSK layer 120 and the second TCO layer 130 that is filled with the encapsulant 135. The P3 scribe isolates the second TCO layer 115 between neighboring perovskite segments, forming segments that can be integrated into the solar cell 200.

The scribe line features P1-P3 can be fabricated by one or more lithography operations (e.g., laser scribing) at various steps in the manufacturing process of the perovskite solar cell 200. Note, if the perovskite solar cell 200 is utilized in a tandem silicon-perovskite solar cell, the encapsulant 135 can be laminated between the perovskite solar cell and a silicon solar cell to form the tandem silicon-perovskite cell, e.g., the tandem cell 100 of FIG. 1A.

FIG. 3 is a flowchart of a fabrication process 300 for forming a perovskite photovoltaic, e.g., the perovskite solar cell 200 of FIG. 2. The process 300 includes generating a substrate supporting a first transparent conducting layer and a hole transport layer (310). In some cases, a pre-formed substrate may instead be provided.

Operation 310 includes providing a substrate (311). The substrate may be a transparent substrate. The substrate may include a silicon-based glass (e.g., an amorphous silicon dioxide, a doped silicon dioxide, etc.), a transparent conductive oxide, a ceramic, a chalcogenide glass, a polymer (e.g., a transparent plastic, poly (methyl methacrylate), etc.), or the like, or any combination thereof. The substrate may include a top surface of a solar cell. For example, the substrate may be a top glass sheet of a silicon solar panel assembly. The substrate may be textured and/or patterned. For example, the substrate may include nano-scale texturing configured as an antireflective coating and an adhesion surface. In another example, the substrate may include patterning configured to generate photonic channels. In another example, the substrate may include pre-patterned portions with electrodes for removing energy from the solar cell (e.g., a top contact grid layout). The substrate may have an area of at least about 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 25, or more square meters. The substrate may have an area of at most about 25, 20, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.5, 0.1, or fewer square meters. The substrate may be a large format substrate. For example, the substrate can be a 10th generation substrate.

Operation 310 includes applying one or more first transparent conductive materials to the substrate to form a first transparent conducting layer (312). The first transparent conducting layer may include a transparent conductive oxide (e.g., indium tin oxide (ITO), indium zinc oxide, aluminum zinc oxide, indium cadmium oxide, etc.), a transparent conductive polymer (e.g., poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), poly(4,4-dioctyl cyclopentadithiophene), etc.), carbon nanotubes, graphene, nanowires (e.g., silver nanowires), metallic grids (e.g., grid contacts including metals), thin films (e.g., thin metal films), conductive grain boundaries, or the like, or any combination thereof. The first

transparent conducting layer may have a full spectrum transparency of at least about 20%, 30%, 40%, 50%, 60%, 70%, 75%, 80%, 85%, 90%, 95%, 96%, 97%, 98%, 99%, 99.9%, or more. The first transparent conducting layer may have a full spectrum transparency of at most about 99.9%, 99%, 98%, 97%, 96%, 95%, 90%, 85%, 80%, 75%, 70%, 60%, 50%, 40%, 30%, 20%, or less. The first transparent conducting layer may have a full spectrum transparency in a range as defined by any two of the proceeding values. For example, the first transparent conducting layer can have a full spectrum transparency of 75% to 85%. The first transparent conducting layer may have a transparency over a spectral band of at least about 20%, 30%, 40%, 50%, 60%, 70%, 75%, 80%, 85%, 90%, 95%, 96%, 97%, 98%, 99%, 99.9%, or more. The first transparent conducting layer may have a transparency over a spectral band of at most about 99.9%, 99%, 98%, 97%, 96%, 95%, 90%, 85%, 80%, 75%, 70%, 60%, 50%, 40%, 30%, 20%, or less. For example, the first transparent conducting layer can have a transmission of 85% over the wavelength range from 400 nm to 1200 nm. The first transparent conducting layer can function as a barrier to the perovskite layer for moisture, gas, dust, and the like. The first transparent conducting layer can also prevent the diffusion of ions (e.g., metal ions) which may impact the performance of the perovskite layer.

Operation 310 includes applying a hole transport layer to the first transparent conducting layer (313). The hole transport layer is configured to shuttle holes from an absorbing layer to the first transparent conducting layer and out of the solar cell. The hole transport layer may include organic molecules (e.g., 2, 2', 7,7'- Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD)), inorganic oxides (e.g., nickel oxide (NiOx), copper oxide (CuOx), cobalt oxide (CoOx), chromium oxide (CrOx), vanadium oxide (VOx), tungsten oxide (WOx), molybdenum oxide (MoOx), copper aluminum oxide (CuAlO2), copper chromium oxide (CuCrO2), copper gallium oxide (CuGaO2), etc.), inorganic chalcogenides (e.g., copper iodide (Cui), copper indium sulfide (CuInS2), copper zinc tin sulfide (CuZnSnS4), cupper barium tin sulfide (CuBaSnS4), etc.) other inorganic materials (e.g., copper thiocyanate (CuSCN), etc.), organic polymers, or the like, or any combination thereof. For example, a glass substrate covered in indium tin oxide can be coated with nickel oxide to form a hole transport layer on the transparent conducting layer.

Operation 310 optionally includes performing one or more lithography operations on the hole transport layer (314). The one or more lithography operations may include optical lithography (e.g., (extreme) ultraviolet lithography, x-ray lithography, laser scribing, etc.), electron beam lithography, ion beam lithography, nanoimprint lithography, other direct

writing processes (e.g., dip-pen lithography, inkjet printing), or the like, or any combination thereof. For example, a number of features (e.g., P1 scribe features) can be inscribed onto the hole transport layer and the underlying first transparent conducting layer using a laser scribe. The one or more lithography operations may include the addition and/or subtraction of features. For example, features can be cured and made permanent. In another example, features can be formed by the removal of material from the target.

The process 300 includes applying a layer of a perovskite precursor to the hole transport layer (320). The precursor is applied using solvent coating technique described below with references to FIGS. 4A-4D. The process 300 optionally includes applying one or more additional perovskite precursors to the hole transport layer (330). The additional perovskite layers may be applied using a solvent coating method or some other method. For example, the subsequent perovskite layer can be deposited by chemical vapor deposition (CVD), plasma enhanced CVD, atomic layer deposition, spin coating, dip coating, drop casting, centrifugal casting, sol-gel deposition, plating, physical vapor deposition, thermal evaporation, molecular beam epitaxy, sputtering, pulsed laser deposition, cathodic arc deposition, ultrasonic spray-on, or inkjet printing. Generally, the one or more perovskite precursors may include one or more lead halides (e.g., lead fluoride, lead chloride, lead bromide, lead iodide, etc.), lead salts (e.g., lead acetates, lead oxides, etc.), other metal salts (e.g., manganese halides, tin halides, metal oxides, metal halides, etc.), organohalides (e.g., formamidinium chloride, formamidinium bromide, formamidinium iodide, methylammonium chloride, methylammonium bromide, methylammonium iodide, butylammonium halides, etc.), alkali metal salts (e.g., alkali metal halides, etc.), alkali earth metal salts (e.g., alkali earth metal halides, etc.), perovskite nanoparticles, or the like, or any combination thereof. A number of perovskite precursors can be used as the one or more perovskite precursors. For example, both methylammonium iodide and butylammonium iodide can be used as perovskite precursors. In this example, the methylammonium iodide can be at about a 1:99, 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 10:90, or 99:1 ratio with the butylammonium iodide. In another example, mixtures of lead halides can be used as a portion of the perovskite precursors. Using different mixtures of lead halides may permit tuning of the bandgap of the perovskite layer. For example, using different mixtures of lead (II) bromide and lead (II) iodide can result in different bandgaps. Using different amounts of lead (II) chloride can affect the crystal stability of the perovskite layer and can prevent phase segregation within the layer. The amount of lead (II) chloride added may be greater than the amount of lead (II) bromide added by weight. The amount of lead (II) chloride added may be

less than the amount of lead (II) bromide added by weight. The amount of lead (II) chloride added may be the same as the amount of lead (II) bromide added by weight. The amount of lead (II) iodide soluble in a solution may be related to the amount of lead (II) bromide and lead (II) chloride in the solution. For example, adding in more lead (II) bromide and lead (II) chloride to a solution of lead (II) iodide can improve solubility of the lead (II) iodide and result in decreased particulate in the perovskite layer.

The solution generally includes a mixture of co-solvents. Examples of solvents include, but are not limited to, polar solvents (e.g., water, dimethyl sulfoxide, dimethylformamide, ethers, esters, acetates, acetone, etc.), non-polar solvents (e.g., hexanes, toluene, etc.), or the like, or any combination thereof. Proper mixing of the solvent as well as solvent composition can contribute to controlled solvent removal speeds and thus impact grain development as well as bulk defect formation. Tuning the interaction of the coordination strength of a solvent and the evaporation rate of a precursor solution can enable better control of the perovskite film that is formed as well as the reaction kinetics of the formation. For example, a weakly coordinating solvent that quickly evaporates may form a more disordered film but may also result in less residual solvent being present in the film. Mixtures of solvents can improve solute solubility, decrease evaporation rates, improve performance of application methods, and the like. For example, a combination of NMP and DMSO can increase solute solubility and decrease solvent evaporation rates. In this example, the properties of the NMO/DMSO mixture can decrease premature crystallization of perovskite and improve film quality. In another example, adding NMP to DMF can increase spray width of the solution through an ultrasonic spray on apparatus, which can provide greater flexibility in the spray on parameters used.

The perovskite precursor solution may include one or more additives. The addition of the additives may reduce and/or eliminate defects within perovskite layers as prepared elsewhere herein. The additives may include one or more recrystallization solvents. The recrystallization solvents may be added to the solution including the one or more perovskite precursors. The recrystallization solvents may be applied after deposition of the one or more perovskite precursors and/or after an annealing of the one or more perovskite precursors. For example, a lead halide precursor can be applied and subsequently a recrystallization solvent can be applied, and the perovskite precursors can be further annealed to orient the lead halide precursor for better methylammonium iodide integration. Examples of recrystallization solvents include, but are not limited to, halobenzenes (e.g., chlorobenzene, bromobenzene,

etc.), haloforms (e.g., chloroform, iodoform, etc.), ethers (e.g., diethyl ether), or the like, or any combination thereof.

A variety of parameters may be tuned to provide a predetermined perovskite layer. Examples of parameters include, but are not limited to, perovskite precursor solution application temperature, volume application rate, ultrasonic power of an ultrasonic spray-on instrument, lateral speed of precursor application (e.g., the speed of a substrate moving through an applicator), applicator height (e.g., the distance from an applicator to the substrate, environmental factors (e.g., humidity, reactive gas content, temperature, etc.), wetting surface energy, or the like, or any combination thereof. Any portion of process 300, including the application of the perovskite precursors, may take place in a controlled environment. The controlled environment may have a relative humidity of at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 99%, or more. The controlled environment may have a relative humidity of at most about 99%, 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10%, or less. The controlled environment may include a controlled atmosphere. The controlled atmosphere may include inert gasses (e.g., nitrogen, noble gases, etc.). The controlled atmosphere may have an oxygen content of at least about 1 part per million (ppm), 10 ppm, 50 ppm, 100 ppm, 500 ppm, 1,000 ppm, 5,000, ppm, 1%, 5%, 10%, 15%, 20%, or more. The controlled atmosphere may have an oxygen content of at most about 20%, 15%, 10%, 5%, 1%, 5,000 ppm, 1,000 pm, 500 ppm, 100 ppm, 50 ppm, 10 ppm, 1 ppm, or less. The controlled atmosphere may be at a temperature of at least about 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 160, 170, 180, 190, 200, or more degrees Celsius. The controlled atmosphere may be at a temperature of at most about 200, 190, 180, 170, 160, 150, 145, 140, 135, 130, 125, 120, 115, 110, 105, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, or less degrees Celsius.

The process 300 includes performing one or more processing operations to the perovskite precursors to generate a perovskite layer (340). Operation 340 includes providing a substrate supporting a first transparent conducting layer, a hole transport layer, and one or more applied perovskite precursors (341). The substrate may be a result of operations 310 - 330 of process 300.

Operation 340 includes performing processing operations on the perovskite precursors to generate a perovskite layer (342). The processing operations may include annealing, light exposure (e.g., ultraviolet light exposure), agitation (e.g., vibration), functionalization (e.g., surface functionalization), electroplating, template inversion, or the like, or any combination thereof. For example, a substrate with perovskite precursors can be annealed to form a

perovskite layer from the precursors. In another example, perovskite precursors can be annealed and subsequently functionalized. The annealing may be annealing under inert atmosphere (e.g., argon atmosphere, nitrogen atmosphere). The annealing may be under a reactive atmosphere (e.g., an atmosphere including a reagent (e.g., methylammonium)). The annealing may be at a temperature of at least about 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 160, 170, 180, 190, 200, or more degrees Celsius. The annealing may be at a temperature of at most about 200, 190, 180, 170, 160, 150, 145, 140, 135, 130, 125, 120, 115, 110, 105, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, or less degrees Celsius. The annealing may be at a temperature range as defined by any two of the proceeding values. For example, the annealing can be at a temperature of 90 to 120 degrees Celsius. The annealing may be for a time of at least about 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 75, 90, 105, 120, or more minutes. The annealing may be for a time of at most about 120, 105, 75, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.5, or less minutes. The annealing may be for a time range as defined by any two of the proceeding values. For example, the annealing can be for a time of about 5 to about 15 minutes. There may be a number of annealing processes applied to the substrate. For example, a substrate can be annealed at a first time and temperature, and subsequently annealed again at a second time and temperature. Such additional annealing processes can reduce the number of defects present in the perovskite layer and improve performance.

Operation 340 optionally includes applying one or more additional layers to the perovskite layer (343). The one or more additional layers may include one or more additional perovskite layers. For example, a second perovskite layer with a different bandgap can be applied to the first perovskite layer. The one or more additional layers may include one or more additional perovskite precursors. For example, iodine gas can be applied to form an iodine layer on a perovskite and/or perovskite precursor layer. The one or more additional layers may include one or more washing operations. A washing operation may include an application of a solvent to the perovskite layer. Examples of solvents include, but are not limited to, water, non-polar organic solvents (e.g., hexanes, toluene, etc.), polar organic solvents (e.g., methanol, ethanol, isopropanol, acetone, etc.), ionic solvents, or the like. The one or more additional layers may include one or more passivating layers. A passivating layer may include a reagent configured to passivate and/or stabilize the perovskite layer. For example, an application of a solution including phenethylammonium iodide can passivate and stabilize the grains of the perovskite layer.

Operation 340 optionally includes performing one or more lithography operations on the one or more additional layers and/or the perovskite layer (344). The one or more lithography operations may be one or more lithography operations as described elsewhere herein. For example, a laser scribe can be used to generate features (e.g., P2 scribe features) on the perovskite layer and one or more of the underlying layers.

The process 300 includes applying an electron transport layer (ETL) to the perovskite layer (350). Operation 350 includes providing a substrate supporting a first transparent conducting layer, a hole transport layer, and a perovskite layer (351) The ETL may be applied by methods and systems as described elsewhere herein (e.g., physical vapor deposition, ultrasonic spray-on, etc.). The electron transport layer may include a material with a conduction band minimum less than that of the perovskite layer. For example, if the perovskite layer has a conduction band minimum of -3.9 eV, the electron transport layer may have a conduction band minimum of -4 eV. Examples of electron transport layer materials include, but are not limited to, titanium oxide (e.g., TiO_2), zinc oxide, tin oxide, tungsten oxide, indium oxide, niobium oxide, iron oxide, cerium oxide, strontium titanium oxide, zinc tin oxide, barium tin oxide, cadmium selenide, indium sulfide, lead iodide, organic molecules (e.g., phenyl-C61 -butyric acid methyl ester (PCBM), poly(3- hexylthiophene-2,5-diyl) (P3HT), etc.), lithium fluoride, buckminsterfullerene (C60), or the like, or any combination thereof.

Operation 350 optionally includes performing one or more lithography operations on the electron transport layer (353). The one or more lithography operations may be one or more lithography operations as described elsewhere herein. For example, a laser scribe can be used to generate features on the electron transport layer and one or more of the underlying layers.

The process 300 includes applying a second transparent conducting layer to the ETL (360). The second transparent conducting layer may be of the same type as the first transparent conducting layer. For example, both the first and second transparent conducting layers may be indium tin oxide. The second transparent conducting layer may be of a different type as the first transparent conducting layer. The second transparent conducting layer may be deposited as described elsewhere herein (e.g., physical vapor deposition, etc.).

Operation 360 optionally includes applying one or more busbars to the second transparent conducting layer (363). The one or more busbars may be applied as busbars (e.g., preformed busbars are applied to the second transparent conducting layer). For example, a mask can be used to form the busbars from an evaporation process. The one or more busbars

may be applied as a solid film and subsequently formed into the busbars. For example, a silver film can be deposited onto the second transparent conducting layer and etched to form the busbars. In another example, a laser scribe can be used to form the busbars from a silver film.

Operation 360 optionally includes performing one or more lithography operations on the electron transport layer (364). The one or more lithography operations may be one or more lithography operations as described elsewhere herein. For example, a laser scribe can be used to generate features (e.g., P3 scribe features) on the second transparent conducting layer and one or more of the underlying layers.

The busbars may be attached to at least about 2, 3, 4, or more terminals. The terminals may be configured to form a parallel connection with one or more additional photovoltaic cells. The terminals may be configured to form a series connection with one or more additional photovoltaic cells. The terminals may be scribed (e.g., laser scribed). The terminals may be configured to enable connection of a perovskite photovoltaic device with another photovoltaic device prior to a lamination of the two photovoltaic devices. For example, a perovskite photovoltaic device can be connection via two terminals to a silicon photovoltaic device.

The process 300 includes applying an encapsulant to the second transparent conducting layer (370). The encapsulant may be applied to the first transparent conducting layer as well as the second transparent conducting layer. For example, the encapsulant can be supported between the substrate and the first transparent conducting layer. The encapsulant may be applied across the second transparent conducting layer (e.g., applied to the whole layer), to a portion of the second transparent conducting layer (e.g., a portion of the layer), to the edges of the second transparent conducting layer (e.g., as a seal over the entire stack of layers), or the like, or any combination thereof. For example, the encapsulant can be applied on the edge (e.g., as an edge seal) of the full stack of layers to prevent moisture and oxygen diffusion into the stack. The encapsulant may be configured to reduce or substantially eliminate an exposure of the perovskite layer to one or more reactive species. The encapsulant may be substantially transparent. For example, the encapsulant may be transparent in a same region of light as the second transparent conducting layer. The encapsulant may have refractive indices similar to the second transparent conducting layer. The encapsulant may be configured to reduce or substantially eliminate an exposure of the perovskite layer to one or more reactive species. Examples of reactive species include, but are not limited to, oxygen, water, and polar molecules (e.g., polar volatile organic compounds,

acids, etc.). Examples of encapsulants include, but are not limited to, PDMS, HelioSeal™, silicon glue, butyl-based sealants, or the like. If used for edge encapsulation as an edge seal, the encapsulant may include tape. The tape may be an adhesive backed barrier. The encapsulant may be placed such that the encapsulant ends at least about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, or more millimeters from the edge. The encapsulant may be place such that the encapsulant ends at most about 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, or fewer millimeters from the edge.

FIGS. 4A-4D show steps in an example process for forming a layer of a perovskite material by solvent coating a perovskite precursor onto a substrate stack in a single coating step. These steps can correspond to steps 320 and 340 described above. The substrate is composed of a glass layer 405, a TCO layer 410, and a charge transport layer 415 (e.g., a HTL or an ETL). In certain examples, the charge transport layer 415 is a layer of NiO_x, an HTL. The substrate can be a large area substrate. For example, the substrate can be 30 cm x 30 cm, or larger (e.g., 1,000 cm^2 or more, e.g., 5,000 cm^2 or less, e.g., 200 cm x 100 cm).

Referring to FIG. 4A, the substrate is coated with a solution containing the perovskite precursor by moving the substrate relative to a coating head 401 (as indicated by the arrow). Generally, coating head 401 can be a head of any appropriate coater, such as a blade coater or a slot die coater. The coating station can move the substrate relative to a stationary coating head, move a coating head relative to a stationary substrate, or move both the substrate and the coating head. The coating parameters (e.g., velocity, displacement of the head from the substate surface, etc.) are generally selected so that the coating is of a desired thickness and uniformity. In some examples, the coating has a thickness in a range from 500 nm to 5,000 nm (e.g., 750 nm, 1,000 nm, 1,250 nm, 1,500 nm, 2,000 nm, 2,500 nm, or more, e.g., 4,000 nm, 3,000 nm, 2,500 nm, 2,000 nm, 1,500 nm, or less).

The solution is composed of a multi-component perovskite precursor and a mixture of solvents. The perovskite precursor can include components described below. In some examples, the perovskite precursor includes a mixture composed of one or more of: a metal halide and organohalides selected from the group consisting of formamidinium chloride, formamidinium bromide, formamidinium iodide, methylammonium chloride, methylammonium bromide, methylammonium iodide, and butylammonium halides.

The solvent mixture includes solvents with different vapor pressures so that they evaporate at different rates. Generally, at a given temperature, a solvent with a lower vapor pressure will evaporate more quickly than a solvent with a higher vapor pressure. It is

believed that the utilizing solvent mixtures with components having different evaporation rates can control crystallization rates of the perovskite material and thereby influence the quality of the perovskite material. In some examples, the solvent mixture can include at least one component solvent with a vapor pressure at 20 °C of 20 mm Hg or less (e.g., 15 mm Hg, 12 mm Hg, 10 mm Hg, 8 mm Hg, 5 mm Hg, 4 mm Hg, 3 mm Hg, or less). The solvent mixture can also include at least one component with a vapor pressure at 20 °C of 60 mm Hg or more (e.g., 70 mm Hg, 80 mm Hg, 90 mm Hg, 100 mm Hg, 110 mm Hg, 120 mm Hg, 130 mm Hg, 140 mm Hg, 150 mm Hg, or more).

In some examples, the solvent mixture includes, as a component with a relatively low vapor pressure, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N, N′-dimethylpropyleneurea (DMPU), and/or n-methyl-2-pyrrolidinone (NMP). In certain examples, the solvent mixture includes, as a component with a relatively high vapor pressure, tetrahydrofuran (THF) and/or acetonitrile (ACN).

Generally, the ratio of the first solvent(s) (having a relatively low vapor pressure) to the second solvent(s) (having a relatively high vapor pressure) in the solvent mixture can vary depending, at least, on the desired evaporation rate of the mixture. In some examples, a ratio by volume of the first solvents to the second solvents is 1:1. In certain examples, the volume of the first solvent is less than the second solvent. For example, the ration can be 2:3 or more (e.g., 1:2 or more, 1:3 or more, 1:4 or more, 1:5 or more, e.g., 1:10 or less, 1:8 or less, 1:6 or less, 1.5 or less).

The concentration of the precursors in the solution is also selected in combination with the solution composition to provide a coating solution that has a desired viscosity suitable for forming a uniform coating of desired thickness using the coater. Generally, the concentration can be in a range from 0.3 M to 3 M, depending on the implementation. In some examples, the precursor concentration is in a range from 0.5 M to 2.5 M (e.g., 0.6 M or more, 0.7 M or more, 0.75 M or more, 0.8 M or more, e.g., 2.5 M or less, 2.0 M or less, 1.5 M or less, 1.25 M or less, 1.1 M or less, 1.0 M or less, 0.9 M or less, 0.85 M or less).

The coating can be applied under ambient conditions (ambient temperature, ambient atmosphere). Alternatively, in certain examples, the coating can be applied in a controlled environment, e.g., with controlled temperature, atmosphere, pressure, and/or relatively humidity). In some examples, the coating is applied at a temperature in a range from 20 °C to 40 °C, e.g., room temperature, e.g., 25 °C to 35 °C, e.g., 30 °C to 33 °C. In certain

examples, the coating is applied to a heated substrate (e.g., hot-casting). In such examples, the substrate can be heated to a temperature in a range from 50 °C to 100 °C.

Referring to FIG. 4B, the result of the coating step is a layer 420 of the solution substantially covering the surface of the charge transport layer 415. The layer 420, ideally, is uniform in composition and thickness. The coating thickness and solution composition is selected so that, after solvent removal, the resulting film has a desired thickness. The coating thickness can be in a range from 0.5 μm to 20 μm (e.g., 1 μm, 2 μm, 3, μm, 4 μm, 5 μm, 6 μm, 7 μm, 8 μm, 9 μm, 10 μm, e.g., 18 μm, 15 μm, 12 μm, 10 μm, 9 μm, 8 μm, 7 μm, or less).

To facilitate solvent removal, the coated substrate is exposed to a gas knife 402 (e.g., an air knife). Examples of gas knives and assemblies that use gas knives to facilitate solvent evaporation are described in Provisional Application No. 63/611,408, titled "DRYING AND CRYSTALLIZING PEROVSKITE LAYERS FROM SOLVENT COATED FILMS," and filed December 18, 2023, the entire contents of which is incorporated herein by reference. Solvent removal reduces the coating layer 420 thickness, providing a layer 425 of perovskite precursor. Generally, the operating parameters of the gas knife 402 are selected to remove the solvent at a desired rate that results in layer 420 having a uniform thickness and composition across the substrate. The gas knife station moves the substrate relative to the gas knife 402 so that the coating layer 420 is exposed to a jet of gas which facilitates solvent removal from the coating. The relative velocity of the substate relative to the gas knife 402 can be in a range from 1 mm/s to 100 mm/s (e.g., 2 mm/s, 3 mm/s, 4 mm/s, 5 mm/s, 6 mm/s, 7 mm/s, 8 mm/s, 9 mm/s, 10 mm/s, 20 mm/s, 30 mm/s, 50 mm/s, or more, e.g., 80 mm/s, 60 mm/s, 50 mm/s, 40 mm/s, 30 mm/s, 20 mm/s, 10 mm/s, 8 mm/s, 6 mm/s, or less). The gas pressure of the gas knife 402 can be in a range from 10 PSI to 100 PSI (e.g., 20 PSI, 30 PSI, 40 PSI, or more, e.g., 75 PSI, 60 PSI, 50 PSI, 40 PSI, or less).

After solvent removal, layer 420 is annealed by exposure to heat as illustrated in FIG. 4D. Generally, the layer 420 is annealed at a temperature, in an atmosphere, and for a duration selected to provide a perovskite layer with properties optimized for device performance (e.g., to satisfy established threshold performance parameters). The physical properties influenced by the anneal can include homogeneity of the perovskite material, grain size, layer thickness, etc.

In certain examples, the layer 420 is annealed at a temperature in a range from 40 °C to 150 °C (e.g., 50 °C or more, 60 °C or more, 70 °C or more, 80 °C or more, 90 °C or more,

100 °C or more; e.g., 150 °C or less, 140 °C or less, 130 °C or less, 120 °C or less, 110 °C or less, 100 °C or less, 90 °C or less, 80 °C or less). For example, MA-based perovskites can be annealed in a range from 90 °C to 110 °C. FA-based perovskites can be annealed in a range up to 150 °C. The layer 420 can be annealed in air, in an atmosphere that is reactive with respect to the perovskite precursor, or in an atmosphere that is inert with respect to the perovskite precursor. The layer 420 can be annealed in an atmosphere that has low humidity (e.g., RH < 15%). In some examples, the layer 420 is annealed in an atmosphere that has ambient humidity. In certain cases, the annealing atmosphere has a relative humidity of 20% or more (e.g., 25%, 30%, 33%, 35%, 38%, or more, e.g., 50%, 45%, 40%, or less).

The result of the anneal is a layer 430 of a perovskite material extending uniformly over the surface of the charge transport layer 415. In examples, the layer 430 of perovskite material can have a thickness in a range from 100 nm to 1,500 nm (e.g., 200 nm, 300 nm, 400 nm, 500 nm, 600 nm, 700 nm, 800 nm, 900 nm, 1,000 nm, or more, e.g., 1,200 nm, 1,000 nm, 900 nm, 800 nm, 700 nm, 600 nm, 500 nm, or less).

Generally, the composition of the perovskite material can be any of the perovskites described below. In some examples, the perovskite material $MA_{n1}FA_{n2}Cs_{n3}PbX_3$, where MA is methylammonium, FA is formamidinium, Cs is Cesium, Pb is lead, and X is selected from the group consisting of fluorine, chlorine, bromine, and iodine, wherein n1, n2, and n3 are independently greater than 0 and less than 1. n1 + n2 + n3 can be equal to 1. In some examples, the perovskite can include Rubidium.

It is believed that the use of a solvent mixture as described above can provide a perovskite layer that has higher uniformity and/or a lower pinhole density than a comparable layer formed from a solution that does not contain such solvent mixtures.

FIG. 5 is a flowchart of an example fabrication process 500 for forming a tandem solar module. The process 500 includes providing a silicon solar panel (910). The silicon solar panel may be a silicon solar panel as described elsewhere herein. For example, the silicon solar panel may be a front contact solar panel, an integrated back contact solar panel, a shingled solar panel, or the like. The silicon solar panel may have at least about 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 72, 75, 80, 85, 90, 95, 96, or more solar cells. The silicon solar panel may have at most about 96, 95, 90, 85, 80, 75, 72, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or less solar cells. In some examples, the silicon solar panel has 60 six-inch solar cells arranged in a 6-by-10 grid. The cells may be connected in series. The cells may each have an open circuit voltage of 0.7 V, for a total open circuit voltage of approximately 42 V.

The process 500 includes fabricating perovskite-on-glass as described elsewhere herein (920). For example, the perovskite-on-glass can be fabricated using the process 300 of FIG. 3. The perovskite-on-glass may have at least about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or more layers. The perovskite-on-glass may have at most about 10, 9, 8, 7, 6, 5, 4, 3, 2, or fewer layers.

The process 900 includes laser scribing the perovskite-on-glass to form perovskite cells or strips (930). The fabricating can include use of fabrication techniques as described elsewhere herein. For example, the fabricating can include use of a laser scribe to define the one or more perovskite solar cells. The perovskite solar cells may be any suitable number of perovskite solar cells. For example, the number of perovskite solar cells in the module may be at least about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99, or more perovskite solar cells. The perovskite solar cells may be at most about 99, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, or fewer perovskite solar cells. The perovskite solar cells can be connected in series, in parallel, or in series/parallel.

Laser scribing can separate the perovskite layer into a number of segments. The segments may be formed into more than one perovskite solar cell. For example, electrical contacts can be applied to the segments to extract charge from the segments.

The laser scribing can generate a number of perovskite cells which, when connected together, have a same or substantially same voltage output as the silicon cell. When the voltage output of the perovskite layer per unit area is known, the perovskite layer can be scribed to form perovskite cells of a size to provide a predetermined voltage. For example, a perovskite layer can be scribed to form five perovskite sub-cells each including 40 perovskite solar cells to match a silicon solar cell that has a same voltage output as the 40 perovskite solar cells. In this example, the five perovskite sub-cells can be connected in parallel to increase the current produced by the perovskite layer while maintaining the voltage match with the silicon cell. Generally, any appropriate number of sub-cells can be scribed.

The process 500 includes connecting the cells of the silicon solar panel to the perovskite solar cells to form a tandem cell (940). The silicon solar panel and the perovskite solar cells may be in a voltage matched configuration. The voltage matched configuration may be as described elsewhere herein. For example, the silicon solar cells can have the same voltage as the perovskite solar cells. The perovskite solar cells may be connected to one another in parallel. The perovskite solar cells may be connected to one another in series. The perovskite solar cells may be connected such that there are a number of cells in the perovskite

layer. For example, rows of the perovskite solar cells can be each connected in series and the connected rows can be connected in parallel. The silicon solar panel and the perovskite solar panel may be connected as described elsewhere herein. For example, the perovskite solar cells can be connected via copper (or another metal, charge collection tape, etc.) terminals to the same junction box as the silicon solar cells.

The process 500 includes encapsulating the cells (950). The encapsulating may include applying an encapsulant as described elsewhere herein. For example, the encapsulating can include applying a thermal-plastic polyolefin to the perovskite layer.

The process 500 can include applying contacts to the perovskite solar cells to electrically couple the cells. The contacts may be applied using one or more processes as described elsewhere herein. For example, the contacts can be evaporated onto the perovskite solar cells. In another example, the contacts can be lithographically applied to the perovskite solar cells. The process 900 may include applying an encapsulant to the one or more perovskite solar cells. The applying may be as described elsewhere herein. For example, the encapsulant can be applied via evaporation. In another example, the encapsulant can be spread as a viscous solution onto the perovskite solar cell. The encapsulant may be as described elsewhere herein. For example, the encapsulant may be a thermal-plastic polyolefin. The process 900 may include applying an edge seal to the one or more perovskite solar cells. The edge seal may be as described elsewhere herein. For example, the edge seal can be HelioSeal™.

The silicon solar panel and the perovskite solar panel can be electronically coupled to a same junction box. Such coupling to the same junction box can allow for simple integration of the perovskite layer into existing silicon solar cells. Such coupling can also provide for simple installation of the tandem solar cell, as there can be a single output from the tandem cell instead of multiple outputs. Examples of different electrical network connections for different types of silicon-perovskite hybrid solar cells is described in WO Patent Application No. 2022/066707 A1.

In general, the perovskite layers described herein may have a composition of $MA_{n1}FA_{n2}Cs_{n3}PbX_3$, where MA is methylammonium and FA is formamidinium. n_1, n_2, and n_3 may independently be greater than 0 and/or less than 1. $n_1 + n_2 + n_3$ may equal 1. A perovskite solar cell including said perovskite layer may retain at least about 80% solar conversion efficiency after 300 hours of illumination under one sun conditions in an air atmosphere at 45 °C. The perovskite layer may be used as described elsewhere herein (e.g., used as an absorbing layer for a perovskite photovoltaic).

In the above equation, X may be selected from the group consisting of fluorine, chlorine, bromine, and iodine. For example, X can be iodine. X may be a combination of two or more of fluorine, chlorine, bromine, and iodine. For example, X may be a mixture of chlorine and iodine. The combination may include individual components having a concentration of at least about 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99, or more percent. The combination may include individual components having a concentration of at most about 99, 98, 97, 96, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.5, 0.1 or less percent. For example, the combination may be a mixture of about 1% chlorine and 99% iodine. The combination may include individual components having a concentration in a range as defined by any two of the previous values. For example, the combination can be a mixture of about 1% - 5% bromine and about 95% - 99% iodine.

In the proceeding formula, n_1, n_2, and n_3 may individually be greater than at least about 0.0001, 0.0005, 0.001, 0.005, 0.01, 0.05, 0.1, 0.11, 0.12, 0.13, 0.14, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9, 0.95, 0.96, 0.97, 0.98, 0.99, or more. In the proceeding formula, n_1, n_2, and n_3 may individually be less than at most about 0.99, 0.98, 0.97, 0.96, 0.95, 0.9, 0.85, 0.8, 0.75, 0.7, 0.65, 0.6, 0.55, 0.5, 0.45, 0.4, 0.35, 0.3, 0.25, 0.2, 0.15, 0.14, 0.13, 0.12, 0.11, 0.1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.01, 0.005, 0.001, 0.0005, 0.0001, or less. In the proceeding formula, n_1, n_2, and n_3 may individually have a range as defined by any two of the proceeding values. For example, n_1 can be about 0.001 to about 0.05, n_2 can be about 0.8 to about 0.989, and n_3 can be about 0.01 to about 0.15.

The cations of the formula may be as described above (e.g., methylammonium, formamidinium, cesium, butyl ammonium). Examples of other cations that may be used include, but are not limited to, imidazolium, dimethylammonium, guanidinium, ammonium, methylformamidinium, tetramethyl ammonium, trimethylammonium, rubidium, copper, palladium, platinum, silver, gold, rhodium, ruthenium, sodium, potassium, iron, other inorganic cations, other organic cations, or the like, or any combination thereof. The perovskite layer may not include additional additives. For example, the perovskite layer may not include thiocyanate. In another example, the perovskite layer may not include carbamides. The perovskite layer may be configured to provide high performance and longevity without additional additives. The lack of additional additives may provide lower cost and easier manufacturing of the perovskite layer. The inclusion of the cesium cation (or

an equivalent alternate cation) may improve the thermal stability of the perovskite layer. For example, the presence of cesium can increase the strength of the molecular bonds of the lead halide structure of the perovskite layer. The cesium ions may also have a lower vapor pressure than organic ions, which may contribute to the thermal stability of the perovskite layer. The inclusion of formamidinium may be more resilient to high temperatures due to their increased molecular weight as compared to other organic cations (e.g., methylammonium). Due to a possible intrinsic instability of a pure formamidinium perovskite, including cesium and/or methylammonium cations can improve the crystalline stability while maintaining thermal stability. Adding too many light organic cations (e.g., methylammonium) can reduce thermal stability. Adding a small percentage of butylammonium iodide can improve the quality of the perovskite layer due to the larger molecular structure of butylammonium being better able to fill the gaps in the perovskite crystalline structure to better passivate defects or imperfects within the crystal, which can in turn achieve higher quality or performance perovskite layers.

The perovskite solar cell may be a perovskite solar cell as described elsewhere herein. For example, the perovskite solar cell may be a solar cell formed on a top glass of a silicon solar cell. The perovskite layer may retain at least about 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99, or more percent of the initial conversion efficiency value after 300 hours of illumination under one sun conditions in an air atmosphere at >25 °C and <100 °C. The perovskite layer may retain at most about 99, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 14, 13, 12, 11, 10, or less percent of the initial conversion efficiency value after 300 hours of illumination under one sun conditions in an air atmosphere at >25 °C and <100 °C. The perovskite layer may retain a percent of the initial conversion efficiency value after 300 hours of illumination under one sun conditions in an air atmosphere at >25 °C and <100 °C as defined by any two of the proceeding values.

In another aspect, the present disclosure provides a method. The method may include providing a substrate. A perovskite precursor may be applied to the substrate. The perovskite precursor may be annealed to form a perovskite layer. The perovskite layer may include a composition of $MA_{n1}FA_{n2}Cs_{n3}PbX_3$. MA may be methylammonium. FA may be formamidinium. n_1, n_2, and n_3 may independently be greater than 0 and/or less than 1. $n_1 + n_2 + n_3$ may equal 1. A perovskite solar cell including said perovskite layer may retain at least about 80% solar conversion efficiency after 300 hours of illumination under one sun conditions in an air atmosphere at >25 °C and <100 °C. The perovskite layer may be subjected to an encapsulation lamination process at a temperature of at least about 90 °C.

The temperature of the encapsulation lamination process may be at least about 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 160, 170, 180, 190, 200, or more degrees Celsius. The temperature of the encapsulation lamination process may be at a temperature of at most about 200, 190, 180, 170, 160, 150, 145, 140, 135, 130, 125, 120, 115, 110, 105, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, or less degrees Celsius. The temperature of the encapsulation lamination process may be in a temperature range as defined by any two of the proceeding values. The encapsulation may be as described elsewhere herein.

The perovskite solar cell may be a perovskite solar cell as described elsewhere herein. For example, the perovskite solar cell can be a solar cell formed on a top glass of a silicon solar cell. The perovskite layer may retain at least about 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99, or more percent of the initial conversion efficiency value after 300 hours of illumination under one sun conditions in an air atmosphere at >25 °C and <100 °C. The perovskite layer may retain at most about 99, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 14, 13, 12, 11, 10, or less percent of the initial conversion efficiency value after 300 hours of illumination under one sun conditions in an air atmosphere at >25 °C and <100 °C. The perovskite layer may retain a percent of the initial conversion efficiency value after 300 hours of illumination under one sun conditions in an air atmosphere at >25 °C and <100 °C as defined by any two of the proceeding values. The perovskite layer may retain at least about 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 96, 97, 98, 99, or more percent of the initial conversion efficiency value after the encapsulation lamination process. The perovskite layer may retain at most about 99, 98, 97, 96, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 14, 13, 12, 11, 10, or less percent of the initial conversion efficiency value after the encapsulation lamination process. The perovskite layer may retain an efficiency of the initial conversion efficiency value after the encapsulation lamination process as defined by any two of the proceeding values.

The perovskite precursor may be applied as described elsewhere herein. For example, the perovskite precursor can be applied using an ultrasonic spray-on process. In this example, the precursors can be applied in different spray-on operations (e.g., lead (II) iodide can be applied to a substrate, and methylammonium iodide can be applied to the lead iodide). In another example, the perovskite precursors can be applied in a single operation. In this example, a solution including all of the precursors for the perovskite layer can be applied and annealed to form the perovskite layer. The annealing process may include heating the

perovskite layer to at least about 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 160, 170, 180, 190, 200, or more degrees Celsius. The annealing process may include hating the perovskite layer to at most about 200, 190, 180, 170, 160, 150, 145, 140, 135, 130, 125, 120, 115, 110, 105, 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, or less degrees Celsius. The annealing process may include heating the perovskite layer to a temperature range as defined by any two of the proceeding values.

In general, whenever alternate parameter values are presented in the format "1, 2, 3, 4, 5, or more" or "5, 4, 3, 2, 1, or less", they mean the same as "1 or more, 2 or more, 3 or more, 4 or more, 5 or more," and "5 or less, 4 or less, 3 or less, 2 or less, 1 or less", respectively.

Whenever the term "at least," "greater than," or "greater than or equal to" precedes the first numerical value in a series of two or more numerical values, the term "at least," "greater than" or "greater than or equal to" applies to each of the numerical values in that series of numerical values. For example, greater than or equal to 1, 2, or 3 is equivalent to greater than or equal to 1, greater than or equal to 2, or greater than or equal to 3.

Whenever the term "no more than," "less than," or "less than or equal to" precedes the first numerical value in a series of two or more numerical values, the term "no more than," "less than," or "less than or equal to" applies to each of the numerical values in that series of numerical values. For example, less than or equal to 3, 2, or 1 is equivalent to less than or equal to 3, less than or equal to 2, or less than or equal to 1.

The term "solar cell," as used herein, generally refers to a device that uses the photovoltaic effect to generate electricity from light.

The term "tandem," as used herein, refers to a solar module with two solar cells that are stacked on top of one another.

The term "4-terminal," as used herein, refers to a tandem solar module in which the top and bottom solar cells each have two accessible terminals.

The term "perovskite," as used herein, generally refers to a material with a crystal structure similar to calcium titanium oxide and one that is suitable for use in perovskite solar cells. The general chemical forum for a perovskite material is ABX3. Examples of perovskite materials include methylammonium lead trihalide (i.e., CEENHaPbX3, where X is a halogen ion such as iodide, bromide, or chloride) and formamidinium lead trihalide (i.e., EENCElNEhPbX3, where X is a halogen ion such as iodide, bromide, or chloride).

The term "monocrystalline silicon," as used herein, generally refers to silicon with a crystal structure that is homogenous throughout the material. The orientation, lattice

parameters, and electronic properties of monocrystalline silicon may be constant throughout the material. Monocrystalline silicon may be doped with phosphorus or boron, for example, to make the silicon n-type or p-type respectively.

The term "polycrystalline silicon," as used herein, generally refers to silicon with an irregular grain structure.

The terms "passivated emitter rear contact (PERC) solar cell," as used herein, generally refer to a solar cell with an extra dielectric layer on the rear-side of the solar cell. This dielectric layer may act to reflect unabsorbed light back to the solar cell for a second absorption attempt and may additionally passivate the rear surface of the solar cell, increasing the solar cell's efficiency.

The terms "heterojunction with intrinsic thin layer solar cell (HIT) solar cell," as used herein, generally refer to a solar cell that is composed of a monocrystalline silicon wafer surrounded by ultra-thin amorphous silicon layers. One amorphous silicon layer may be n-doped, while the other may be p-doped.

The term "an interdigitated back contact cell (IBC)," as used herein, generally refers to a solar cell including two or more electrical contacts disposed on the back side of the solar cell (e.g., on the side opposite the incident light). The two or more electrical contacts can be disposed adjacent to alternatingly n- and p-doped regions of the solar cell. An IBC can include a high-quality absorber material configured to permit carrier migration over a long distance.

The terms "bandgap" and "band gap," as used herein, generally refer to the energy difference between the top of the valence band and the bottom of the conduction band in a material.

The term "electron transport layer" ("ETL"), as used herein, generally refers to a layer of material that facilitates electron transport and inhibits hole transport in a solar cell. Electrons are majority carriers in an ETL, while holes are minority carriers. An ETL can be made of one or more n-type layers. The one or more n-type layers can include an n-type exciton blocking layer. The n-type exciton blocking layer can have a wider band gap than the photoactive layer of the solar cell (e.g., the perovskite layer) but a conduction band that is closely matched to the conduction band of the photoactive layer. This allows electrons to easily pass from the photoactive layer to the ETL.

The n-type layer can be a metal oxide, a metal sulfide, a metal selenide, a metal telluride, amorphous silicon, an n-type group IV semiconductor (e.g., germanium), an n-type group III-V semiconductor (e.g., gallium arsenide), an n-type group II- VI semiconductor

(e.g., cadmium selenide), an n-type group I- VII semiconductor (e.g., cuprous chloride), an n-type group IV-VI semiconductor (e.g., lead selenide), an n-type group V-VI semiconductor (e.g., bismuth telluride), or an n-type group II-V semiconductor (e.g., cadmium arsenide), any of which can be doped (e.g., with phosphorus, arsenic, or antimony) or undoped. The metal oxide can be an oxide of titanium, tin, zinc, niobium, tantalum, tungsten, indium, gallium, neodymium, palladium, cadmium, or an oxide of a mixture of two or more of such metals. The metal sulfide can be a sulfide of cadmium, tin, copper, zinc or a sulfide of a mixture of two or more of such metals. The metal selenide can be a selenide of cadmium, zinc, indium, gallium or a selenide of a mixture of two or more of such metals. The metal telluride can be a telluride of cadmium, zinc, cadmium or tin, or a telluride of a mixture of two or more of said metals. Alternatively, other n-type materials can be employed, including organic and polymeric electron transporting materials, and electrolytes. Suitable examples include, but are not limited to, a fullerene or a fullerene derivative (e.g., phenyl-C61-butyric acid methyl ester, C60, etc.) or an organic electron transporting material including perylene or a derivative thereof.

The term "hole transport layer" ("HTL"), as used herein, generally refers to a layer of material that facilitates hole transport and inhibits electron transport in a solar cell. Holes are majority carriers in an HTL, while electrons are minority carriers. An HTL can be made of one or more p-type layers. The one or more p-type layers can include a p-type exciton blocking layer. The p-type exciton blocking layer generally has a valence band that is closely matched to the valence band of the photoactive layer (e.g., the perovskite layer) of the solar cell. This allows holes to easily pass from the photoactive layer to the HTL.

The p-type layer can be made of a molecular hole transporter, a polymeric hole transporter, or a copolymer hole transporter. For example, the p-type layer can be one or more of the following: nickel oxide, thiophenyl, phenelenyl, dithiazolyl, benzothiazolyl, diketopyrrolopyrrolyl, ethoxydithiophenyl, amino, triphenyl amino, carbozolyl, ethylene dioxythiophenyl, dioxythiophenyl, or fluorenyl. Additionally or alternatively, the p-type layer can include spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene)), P3HT (poly(3-hexylthiophene)), PCPDTBT (Poly[2,l,3-benzothiadiazole-4,7- diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,l-b:3,4-b']dithiophene-2,6-diyl]]), PVK (poly(N- vinylcarbazole)), poly(3 -hexylthiophene), poly[N,N-diphenyl-4-methoxyphenylamine-4',4"- diyl], sexithiophene, 9,10-bis(phenylethynyl)anthracene, 5,12-bis(phenylethynyl)naphthacene, diindenoperylene, 9,10-diphenylanthracene, PEDOT-TMA, PEDOT:PSS, perfluoropentacene, perylene, poly(p-phenylene oxide), poly(p-phenylene

sulfide), quinacridone, rubrene, 4- (dimethylamino)benzaldehyde diphenylhydrazone, 4-(dibenzylamino) benzaldehyde- N,Ndiphenylhydrazone or phthalocyanines.

In general, the methods and devices of the present disclosure may be used with any solar cells with a perovskite layer. For example, tandem solar modules can include a perovskite solar cell in combination with any other type of solar cell, e.g., a silicon solar cell or CdTe- solar cell. In another example, the tandem solar cell can be a dye sensitized solar cell perovskite solar cell. In a further example, a solar module can be composed only of perovskite solar cells.

The following numbered paragraphs are non-limiting examples of various embodiments of the present disclosure.

1. A method, including: causing relative motion between a substrate and a coating head while delivering a solution from the coating head to a surface of the substrate to form a coating of the solution on the surface, the solution including a mixture of two or more solvents and a perovskite precursor, the two or more solvents including a first solvent having first vapor pressure and a second solvent including a second vapor pressure higher than the first vapor pressure, the second solvent being selected from the group consisting of tetrahydrofuran (THF) and acetonitrile (ACN); and exposing the coating to conditions sufficient to cause the solvents to evaporate from the coating and the perovskite precursor to form a layer of a perovskite material on the surface.

2. The method of paragraph 1, wherein the first solvent is dimethylformamide.

3. The method of paragraph 2, wherein the two or more solvents includes N, N′-dimethylpropyleneurea.

4. The method of paragraph 2, wherein the solution includes dimethylformamide, N, N′-dimethylpropyleneurea, and tetrahydrofuran.

5. The method of paragraph 2, wherein the solution includes dimethylformamide, N, N′-dimethylpropyleneurea, and acetonitrile.

6. The method of any one of the previous paragraphs 1-5, wherein the solution has a perovskite precursor concentration in a range from 0.5 M to 1.5 M (e.g., 0.6 M or more, 0.7 M or more, 0.75 M or more, 0.8 M or more, 1.5 M or less, 1.25 M or less, 1.1 M or less, 1.0 M or less, 0.9 M or less, 0.85 M or less).

7. The method of paragraph 1, wherein a ratio by volume of the second solvent to the other solvents in the mixture is in a range from 1:1 to 1:4.

8. The method of any one of the previous paragraphs 1-7, wherein the substrate includes a layer of a charge transport material, and the solution is delivered to a surface of the charge transport material.

9. The method of paragraph 8, wherein the charge transport material is a hole transport material.

10. The method of paragraph 9, wherein the hole transport material is NiO_x.

11. The method of any one of the previous paragraphs 1-10, wherein the perovskite precursor includes a metal halide and organohalides selected from the group consisting of formamidinium chloride, formamidinium bromide, formamidinium iodide, methylammonium chloride, methylammonium bromide, methylammonium iodide, and butylammonium halides.

12. The method of any one of the previous paragraphs 1-11, wherein the perovskite material MAn1FAn2Csn3PbX3, where MA is methylammonium, FA is formamidinium, Cs is Cesium, Pb is lead, and X is selected from the group consisting of fluorine, chlorine, bromine, and iodine, wherein n1, n2, and n3 are independently greater than 0 and less than 1.

13. The method of paragraph 12, wherein n1 + n2 + n3 = 1.

14. The method of any one of the previous paragraphs 1-13, wherein the layer of perovskite material has a thickness in a range of 1,000 nm or less.

15. The method of paragraph 14, wherein the thickness is in a range from 400 nm to 600 nm.

16. The method of any one of the previous claims 1-15, wherein the solution is delivered in an environment at a temperature in a range from 20 °C to 40 °C.

17. The method of paragraph 16, wherein the solution is delivered in an environment at a temperature in a range from 25 °C to 35 °C.

18. The method of paragraph 17, wherein the solution is delivered in an environment at a temperature in a range from 30 °C to 33 °C.

19. The method of paragraph 1, wherein exposing the coating to the conditions includes moving the coating relative to a gas knife.

20. The method of paragraph 19, wherein the gas knife moves relative to the substrate at a velocity in a range from 2 mm/s to 10 mm/s.

21. The method of paragraph 20, wherein the gas knife moves relative to the substrate at a velocity in a range from 4 mm/s to 6 mm/s.

22. The method of any one of paragraphs 19-21, wherein the gas knife has a pressure in a range from 20 PSI to 40 PSI.

23. The method of paragraph 22, wherein the gas knife has a pressure in a range from 20 PSI to 30 PSI.

24. The method of paragraph 1, wherein exposing the coating to the conditions includes annealing the perovskite precursor after evaporating the solvents.

25. The method of paragraph 1, wherein the layer of perovskite material has a pinhole density lower than a pinhole density of a layer having the same chemistry and formed under the same conditions except that the solution does not include THF or ACN.

26. The method of any one of the previous paragraphs, wherein the substrate has an area of 30 cm x 30 cm or more.

27. The method of paragraph 26, wherein the substrate has an area of 1,000 cm2 or more.

28. The method of paragraph 26, wherein the substrate has an area of 200 cm x 100 cm.

29. The method of paragraph 1, wherein during the relative motion, the substrate is moved while the coating head remains stationary.

30. The method of paragraph 1, wherein during the relative motion, the coating head is moved while the substrate remains stationary.

31. The method of any one of the previous paragraphs 1-30, further including forming a solar cell including the substrate and the layer of perovskite material.

32. The method of any one of the previous paragraphs 1-31, wherein forming the solar cell including depositing a charge transport layer on the layer of perovskite material.

33. The method of paragraph 32, wherein the charge transport layer is an electron transport layer.

34. The method of paragraph 32, wherein forming the solar cell includes attaching the substrate and the layer of perovskite material to a silicon solar cell to provide a tandem solar cell.

35. The method of paragraph 34, wherein the substrate forms a top glass layer of the silicon solar cell.

36. An article, including: a substrate; and a layer of a solution supported by the substrate, the solution including a mixture of two or more solvents and a perovskite precursor, the two or more solvents including a first solvent having first vapor pressure and a

second solvent including a second vapor pressure higher than the first vapor pressure, the second solvent being selected from the group consisting of tetrahydrofuran and acetonitrile.

A number of embodiments are described. Other embodiments are in the following claims.

WHAT IS CLAIMED IS:

1. A method, comprising:

causing relative motion between a substrate and a coating head while delivering a solution from the coating head to a surface of the substrate to form a coating of the solution on the surface,

the solution comprising a mixture of two or more solvents and a perovskite precursor,

the two or more solvents comprising a first solvent having first vapor pressure and a second solvent comprising a second vapor pressure higher than the first vapor pressure, the second solvent being selected from the group consisting of tetrahydrofuran (THF) and acetonitrile (ACN); and

exposing the coating to conditions sufficient to cause the solvents to evaporate from the coating and the perovskite precursor to form a layer of a perovskite material on the surface.

2. The method of claim 1, wherein the first solvent is dimethylformamide.

3. The method of claim 2, wherein the two or more solvents comprises N, N′-dimethylpropyleneurea.

4. The method of claim 2, wherein the solution comprises dimethylformamide, N, N′-dimethylpropyleneurea, and tetrahydrofuran.

5. The method of claim 2, wherein the solution comprises dimethylformamide, N, N′-dimethylpropyleneurea, and acetonitrile.

6. The method of claim 1, wherein the solution has a perovskite precursor concentration in a range from 0.5 M to 1.5 M .

7. The method of claim 1, wherein a ratio by volume of the second solvent to the other solvents in the mixture is in a range from 1:1 to 1:4.

8. The method of claim 1, wherein the substrate comprises a layer of a charge transport material and the solution is delivered to a surface of the charge transport material.

9. The method of claim 8, wherein the charge transport material is a hole transport material.

10. The method of claim 9, wherein the hole transport material is NiO_x.

11. The method of claim 1, wherein the perovskite precursor comprises a metal halide and organohalides selected from the group consisting of formamidinium chloride, formamidinium bromide, formamidinium iodide, methylammonium chloride, methylammonium bromide, methylammonium iodide, and butylammonium halides.

12. The method of claim 1, wherein the perovskite material $MA_{n1}FA_{n2}Cs_{n3}PbX_3$, where MA is methylammonium, FA is formamidinium, Cs is Cesium, Pb is lead, and X is selected from the group consisting of fluorine, chlorine, bromine, and iodine, wherein n1, n2, and n3 are independently greater than 0 and less than 1.

13. The method of claim 12, wherein n1 + n2 + n3 = 1.

14. The method of claim 1, wherein the layer of perovskite material has a thickness in a range of 1,000 nm or less.

15. The method of claim 14, wherein the thickness is in a range from 400 nm to 600 nm.

16. The method of claim 1, wherein the solution is delivered in an environment at a temperature in a range from 20 °C to 40 °C.

17. The method of claim 16, wherein the solution is delivered in an environment at a temperature in a range from 25 °C to 35 °C.

18. The method of claim 17, wherein the solution is delivered in an environment at a temperature in a range from 30 °C to 33 °C.

19. The method of claim 1, wherein exposing the coating to the conditions comprises moving the coating relative to a gas knife.

20. The method of claim 19, wherein the gas knife moves relative to the substrate at a velocity in a range from 2 mm/s to 10 mm/s.

21. The method of claim 20, wherein the gas knife moves relative to the substrate at a velocity in a range from 4 mm/s to 6 mm/s.

22. The method of claim 19, wherein the gas knife has a pressure in a range from 20 PSI to 40 PSI.

23. The method of claim 22, wherein the gas knife has a pressure in a range from 20 PSI to 30 PSI.

24. The method of claim 1, wherein exposing the coating to the conditions comprises annealing the perovskite precursor after evaporating the solvents.

25. The method of claim 1, wherein the layer of perovskite material has a pinhole density lower than a pinhole density of a layer having the same chemistry and formed under the same conditions except that the solution does not include THF or ACN.

26. The method of claim 1, wherein the substrate has an area of 30 cm x 30 cm or more.

27. The method of claim 26, wherein the substrate has an area of 1,000 cm^2 or more.

28. The method of claim 26, wherein the substrate has an area of 200 cm x 100 cm.

29. The method of claim 1, wherein during the relative motion, the substrate is moved while the coating head remains stationary.

30. The method of claim 1, wherein during the relative motion, the coating head is moved while the substrate remains stationary.

31. The method of claim 1, further comprising forming a solar cell comprising the substrate and the layer of perovskite material.

32. The method of claim 1, wherein forming the solar cell comprising depositing a charge transport layer on the layer of perovskite material.

33. The method of claim 32, wherein the charge transport layer is an electron transport layer.

34. The method of claim 32, wherein forming the solar cell comprises attaching the substrate and the layer of perovskite material to a silicon solar cell to provide a tandem solar cell.

35. The method of claim 34, wherein the substrate forms a top glass layer of the silicon solar cell.

36. An article, comprising:

a substrate; and

a layer of a solution supported by the substrate,

the solution comprising a mixture of two or more solvents and a perovskite precursor,

the two or more solvents comprising a first solvent having first vapor pressure and a second solvent comprising a second vapor pressure higher than the first vapor pressure, the second solvent being selected from the group consisting of tetrahydrofuran and acetonitrile.