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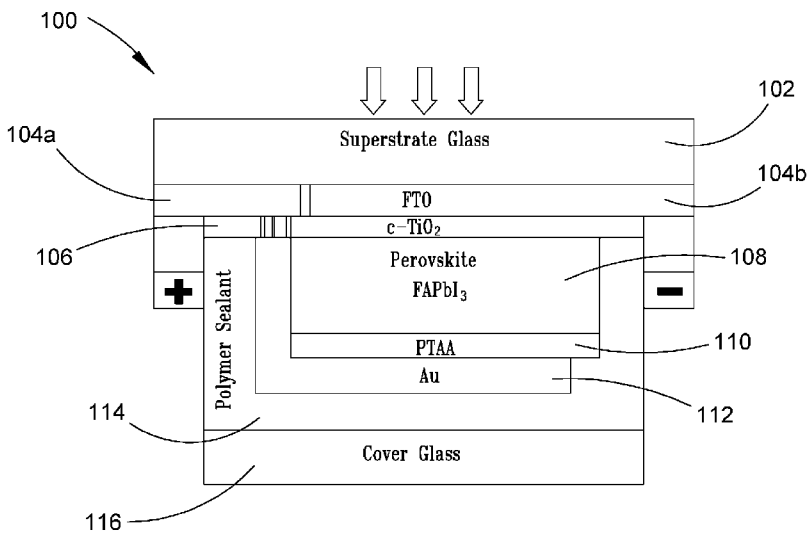

FIGURE 1

(57) Abstract: A photovoltaic device comprising a substrate; a transparent conductive oxide layer in contact with the substrate; an electron transport layer in contact with the transparent conductive oxide layer; a perovskite light-absorbing layer in contact with the electron transport layer; a hole transport layer in contact with the light absorbing layer; an electrode element in electrical contact with the hole transport layer; and an encapsulation layer disposed at the rear of the device being arranged to wrap around a structure comprising the light-absorbing layer, the hole transport layer and the electrode element and to be in continuous contact with the electron transport layer along the entire perimeter of the structure; wherein, in use, electrons generated in the light absorbing layer travel through the electron transport layer to a first portion of the transparent conductive oxide layer before being extracted from the device; and holes generated in the light absorbing layer travel through the hole transport layer to the electrode element and from the electrode element to

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a second portion of the transparent conductive oxide layer before being extracted from the device.

A THIN FILM PHOTOVOLTAIC DEVICE AND A METHOD FOR ENCAPSULATING THE SAME

Field of the Invention

The present invention generally relates to a metal halide photovoltaic device and a method of manufacturing the same, in particular the invention relates to a method of encapsulating a metal halide photovoltaic device.

Background of the Invention

In recent years photovoltaic devices based on metal halide perovskites (PSC) have shown promising performance. Record power conversion efficiencies in the order of 22% make PSC-based devices promising for large scale adoption.

One of the main problems faced by this technology is the relatively poor stability and high sensitivity to operational and environmental conditions, such as high temperature and moisture.

There is a need in the art for a technical solution that allows improving the stability of PSC perovskite based photovoltaic devices.

Summary of the Invention

In accordance with a first aspect, the present invention provides a photovoltaic device comprising:

a substrate;

a transparent conductive oxide layer in contact with the substrate;

an electron transport layer in contact with the transparent conductive oxide layer

a light-absorbing layer comprising a material with a perovskite structure; the light absorbing material being in contact with the electron transport layer;

a hole transport layer in contact with the light absorbing layer such that the light absorbing layer is positioned between the electron transport layer the hole transport layer;

an electrode element in electrical contact with the hole transport layer; and

an encapsulation layer disposed at the rear of the device; the encapsulation layer being arranged to wrap around a structure comprising the light-absorbing layer, the hole transport layer and the electrode element and to be in continuous contact with the electron transport layer along the entire perimeter of the structure;

wherein the transparent conductive oxide layer, the electron transport layer, the hole transport layer and the electrode element are arranged such that, electrons generated in the light absorbing layer travel through the electron transport layer to a first portion of the transparent conductive oxide layer before being extracted from the device; and holes generated in the light absorbing layer travel through the hole transport layer to the electrode element and from the electrode element to a

second portion of the transparent conductive oxide layer before being extracted from the device.

The photovoltaic device may be a planar or mesoporous device.

In embodiments, the first and second portion of the transparent conductive oxide are electrically and/or physically insulated from each other. For example, the first and second portions may be spaced apart from each other and separated by a gap, which may be a void of at least partially filled with an electrically insulating material.

In embodiments, the electron transport layer comprises one or more openings arranged to enable electrical contact between the electrode element and the second portion of the transparent conductive oxide.

In alternative embodiments, the electron transport layer does not have physical openings, however, its thickness is such that holes are able to tunnel from the electrode element to the second portion of the transparent conductive oxide (TCO).

An ohmic contact between the electrode element and a portion of TCO may be made without making a physical opening through the electron transport layer, by reducing the size of the electron transport layer so that it does not fully cover the transparent conductive oxide layer. For example, the glass may be used to shade the future contact area during the deposition of the electron transport layer deposition.

In embodiments, the encapsulation material is such to form a pressurised seal around the structure comprising the light-absorbing layer, the hole transport layer and the electrode element allowing to substantially reduce the velocity of chemical reactions, such as decomposition reactions, in the structure while the photovoltaic device is in use.

Furthermore, the continuous seal formed by the encapsulation layer, allows to prevent environment elements/contaminants such as oxygen and moisture from entering into contact with the structure and be detrimental to active parts of the device.

In embodiments, the encapsulation material comprises polyisobutylene. Alternatively, the encapsulation material may comprise materials that have water permeation rate below 0.1 g*mm/m^2*day at 23°C, 100% R.H., air permeation rate below 1000 cm^3*mm/m^2*day*atm at 80°C, resistivity larger than 10^{10} ohm*cm at 23°C, chemically inert to perovskite photovoltaic device and good adhesion to the hole blocking layer or transparent conductive oxide layer.

The electron transport layer may comprise TiO_2. Furthermore, the hole transport layer may comprise PTAA (poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine])). The electrode element may be made from gold.

In accordance with the second aspect, the present invention provides a method of forming a photovoltaic device; the method comprising the steps of:

providing a substrate comprising a transparent conductive oxide layer;

forming a first and a second portion of the transparent conductive oxide layer by creating an opening in the transparent conductive oxide layer;

forming an electron transport layer onto the transparent conductive oxide layer

forming a light-absorbing layer onto the electron transport layer; the light-absorbing layer comprising a material with a perovskite structure;

forming a hole transport layer onto the light absorbing layer;

forming an electrode element onto the hole transport layer in a manner such that the electrode element is in electrical contact with the hole transport layer and with the second portion of the transparent conductive oxide layer; and

forming an encapsulation layer at the rear of the device in a manner such that the encapsulation layer wraps around a structure comprising the light-absorbing layer, the hole transport layer and the electrode element and to be in continuous contact with the electron transport layer along the entire perimeter of the structure;

wherein the transparent conductive oxide layer, the electron transport layer, the hole transport layer and the electrode element are such that, in use, electrons generated in the light absorbing layer travel through the electron transport layer to the first portion of the transparent conductive oxide layer before being extracted from the device; and holes generated in the light absorbing layer travel through the hole transport layer to

the electrode element and from the electrode element to a second portion of the transparent conductive oxide layer before being extracted from the device.

The photovoltaic device may be a planar or mesoporous device.

In some embodiments, the method further comprises the step of forming one or more openings in the electron transport layer to facilitate electrical contact of the electrode element with the second portion of the transparent conductive oxide.

Advantages of embodiments of the invention provide a thin film perovskite based photovoltaic device with improved stability. The complete encapsulation using a polymeric sealing material, such as a polymeric material comprising PIB (polyisobutylene), PO (polyolefin) or another suitable polymeric material, allows to slow down chemical reaction triggered by temperature while the device is in use and, at the same time, degradation due to moisture entering the device. The complete encapsulation is possible due to the lack of an electrode feed-through which is common in current perovskites solar cells.

Brief Description of the Drawings

Features and advantages of the present invention will become apparent from the following description of embodiments thereof, by way of example only, with reference to the accompanying drawings in which:

Figure 1 and 2 show schematic representations of a photovoltaic devices in accordance with embodiments of the present invention;

Figure 3 there shows a photographic image of a photovoltaic device in accordance with an embodiment of the present invention;

Figures 4 to 7 show a Thermal Cycling / Damp Heat Test plot and Hysteresis Index for devices manufactured in accordance with embodiments of the present invention; and

Figure 8 is a flow diagram of a method of manufacture of a photovoltaic device in accordance with an embodiment of the present invention;

Detailed Description of Embodiments

Embodiments of the present invention relate to photovoltaic devices comprising a light-absorbing layer based on a perovskite crystal structure and a complete encapsulation. Embodiments allow to improve stability of the device by substantially slowing down or preventing outgassing due to material in the absorber layer reacting within the cell due to high temperatures.

The Applicants realised that the poor stability of the perovskite photovoltaic devices is not only related to environmental contamination, but also to degradation of the materials within the device that react due to high temperatures when the devices are in use.

The Applicants engineered a new design for contacting the electron selective membrane of the cell that allows for a complete encapsulation with a low permeability material,

such as PIB or another suitable polymeric material, along the entire perimeter of the active part of the device, without metal feedthroughs.

In the following detailed description, the results obtained by the Applicant for a glass/polymeric sealant/glass encapsulation method are discussed.

Referring now to figure 1, there is shown a schematic representation of a planar photovoltaic device 100 manufactured in accordance with embodiments of the present invention. The device 100 has a substrate 102 on which components of the device 100 is formed. This type of solar cell has a superstrate configuration; therefore the incoming photons enter the device through the substrate.

The substrate 102 has a layer of transparent conductive oxide, such as FTO, which is in in contact with the substrate. The transparent conductive oxide is divided in two portions 104a and 104b, usually by creating a physical opening in the layer.

An electron transport layer 106 is positioned in contact with the transparent conductive oxide (TCO) layer 104. In this embodiment, the layer 106 is made of TiO_2.

A light-absorbing layer 108 comprising a material with a perovskite structure, in this instance $FAPbI_3$, is formed onto a portion of the electron transport layer 106 and is in electrical contact with the electron transport layer 106.

A hole transport layer 110, in this instance made of PTAA, is formed in contact with the light absorbing layer 108 to prevent electrons from crossing from the light absorber

layer 108 towards a metal electrode 112, in this case made of gold, which is used to extract charge carriers from the device.

The components of the device 100 are encapsulated using an encapsulation layer 114 that wraps around the structure comprising the light-absorbing layer 108, the hole transport layer 110 and the electrode element 112. The encapsulation layer 114 is in contact with the electron transport layer 106 along the entire perimeter of the structure. In other words, the encapsulation layer 114 forms a continuous seal, without gaps around the active part of the device 100. The encapsulation layer 114 typically is provided in the form of a polymeric seal and may for example comprise PIB, PO or another suitable polymeric material.

This is in contrast with existing technologies that generally use a metal electrode that feeds through the encapsulation layer to contact the rear of a photovoltaic device. The Applicants found that the feedthrough facilitates the ingress of moisture and contaminants from the outside into the device and prevents pressure sealing of the device allowing for temperature driven reactions to take place inside the device.

To extract the holes from the device without having a metal feedthrough the Applicants have found that an electrical connection can be formed internally, from the gold electrode 112 to the second portion of the FTO 104a. Using this technique, electrons generated in the light absorbing layer 108 travel through the electron transport layer 106 to a first portion of the transparent conductive oxide 104b before being extracted from the device. Holes

generated in the light absorbing layer 108 travel through the hole transport layer 110 to the electrode element 112 and from the electrode element 112 to the second portion of the transparent conductive oxide layer 104a before being extracted from the device.

In alternative embodiments, the contact between the electrode element 112 and the portion of TCO layer 104a can be made without making a physical opening through the electron transport layer 106, by reducing the size of the electron transport layer 106 so that it does not fully cover the transparent conductive oxide layer. For example, glass may be used to shade the contact area during TiO_2 deposition, so that after the deposition of gold, the electrode element 212 is in contact with the TCO 104a directly. In this case, the materials/layers covered by the encapsulant also includes TCO. However, in this embodiment, care must be taken not to contaminate that contact area (Au to TCO) during the deposition processes of other layers (absorber, HTL).

Referring now to figure 2, there is shown a mesoporous type perovskite solar cell device 150 manufactured in accordance with an embodiment of the present invention. The device 150 has a substrate 152 on which components of the device 150 is formed. This type of solar cell has a superstrate configuration; therefore the incoming photons enter the device through the substrate.

The substrate 152 has a layer of transparent conductive oxide, such as FTO, which is in in contact with the substrate. The transparent conductive oxide is divided in two portions 154a and 154b, usually by creating a physical opening in the layer.

An electron transport layer 156 is positioned in contact with the transparent conductive oxide (TCO) layer 154. In this embodiment, the layer 156 comprises a layer of is mesoporous TiO_2 (m-TiO_2) which is deposited on top of a planar compact TiO_2 (c-TiO_2) layer.

A light-absorbing layer 108 comprising a mesoporous-type perovskite material, in this example comprising $Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.55}Br_{0.45}$, is formed on a portion of the electron transport layer 156 and is in electrical contact with the electron transport layer 156.

A hole transport layer 160, in this instance made of PTAA, is formed in contact with the light absorbing layer 158 to prevent electrons from crossing from the light absorber layer 158 towards a metal electrode 162, in this case made of gold, which is used to extract charge carriers from the device.

Similar to the device 100 shown in Figure 1, the components of the device 150 are encapsulated using an encapsulation layer 164 that wraps around the structure comprising the light-absorbing layer 108, the hole transport layer 160 and the electrode element 162. The encapsulation layer 164 is in contact with the electron transport layer 156 along the entire perimeter of the structure and forms a continuous seal. The encapsulation layer 164 typically is provided in the form of a polymeric seal and may for example comprise PIB, PO or another suitable polymeric material.

Referring now to figure 3, there is shown a photographic image of a photovoltaic device 200 manufactured in accordance with the schematic of figure 1. The image is

taken from above the superstrate glass. Importantly the image 200 shows the complete seal of the PIB encapsulation layer 214 across the rear portion of the solar cell and the glass substrate (or superstrate in this instance) 202. Further, image 200 shows the gold electrode element 212.

Importantly, the PIB encapsulation layer 214 is arranged so that the rear of the device is sealed without leaving any air pockets or air gaps between the device and the PIB encapsulation.

The observed PCE (average of $J_{SC} \rightarrow V_{OC}$ and $V_{OC} \rightarrow J_{SC}$ scans) is typically in the range of 8-12% for the fabricated devices. The Applicants performed three accelerated lifetime tests, Damp Heat (DH), Thermal Cycling (TC) and Humidity Freeze (HF), in accordance with IEC61215:2016, which is the widely accepted standard for commercial photovoltaic modules. Exposure of the encapsulated devices to ambient temperature and humidity was also studied. Glass/EVA/glass and glass/UV-cured epoxy/glass encapsulation schemes were also investigated, for comparison.

The FTO coated glass 202 was patterned by Nd:YAG laser scribing and cleaned with Hellmanex solution, isopropanol and UV-ozone. A dense blocking layer of TiO_2 106 was deposited by spray pyrolysis (~50 nm) using 20 mM titanium diisopropoxide bis(acetylacetonate) solution at 450°C.

For making a planar PSC, a 1.2 M $HC(NH_2)_2PbI_3$ solution was prepared by dissolving $HC(NH_2)_2I$ and PbI_2 in dimethylformamide (DMF) at 1:1 mole ratio at room temperature. 0.1g hydriodic acid (57 wt% in water) was added per mL of $HC(NH_2)_2PbI_3$/DMF solution. The perovskite

solution is spread on the TiO_2/FTO and spun at 6500 rpm for 30 sec. using a gas-assisted technique. The films were dried on a hot plate at 160°C for 20 min.

For making a mesoporous PSC, a suspension containing 150 mg/mL Dyesol 30 NR-D TiO_2 paste dispersed in ethanol was spin-coated at 4000 rpm (acceleration of 2000 rpm/s) for 15 s on top of the c-TiO_2 layer to form a mesoporous TiO_2 layer. The substrates were then annealed at 100 °C for 10 min followed by sintering at 500 °C for 30 min. A solution of $Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.55}Br_{0.45}$ with mass fraction = 50 % was prepared by dissolving appropriate amounts of CsI, FAI, FABr, MABr and PbI_2 in a 4:1 mixture by volume of dimethylformamide (DMF) and dimethylsulphoxide at room temperature. The perovskite solution was spread on the TiO_2/FTO and spun at 2000 rpm (acceleration of 200 rpm/s) and 6000 rpm (acceleration of 2000 rpm/s) for 10 and 30 s, respectively. After spinning at 6000 rpm for 10 s, the anti-solvent chlorobenzene was dispensed onto the spinning substrate for about 2 s. The films were dried on a hot plate at 120 °C to 130 °C for 20 min.

A solution containing 10.0 mg PTAA, 7.5 µl of a 170 mg/mL lithium bis(trifluoromethylsulphonyl)imide solution (LiTFSI) in acetonitrile and 4.0 µl 4-tert-butylpyridine (t-BP) in 1.0 ml of toluene was spin-coated on the $HC(NH_2)_2PbI_3$/bl-TiO_2/FTO substrate at 3000 rpm for 30 s. A 100 nm gold electrode 112 was deposited by thermal evaporation. The perovskite 108, HTL 110 and gold layers 112 were masked during their deposition with Kapton tape, Scotch tape and a shadow mask, respectively and processed in a nitrogen filled glovebox. The samples were 33 mm x 25 mm in size, sufficient to provide a 6 mm wide border for

edge sealing around the 13 mm x 13 mm area of the perovskite absorber.

PIB, which is supplied as a tape, was first cut into the desired width and applied to the 1 mm thick cover glass. The cover glass with PIB was then applied over the perovskite solar cell. The whole structure was finally hot-pressed in a vacuum laminator for 10 minutes at 90°C which is sufficiently high to facilitate the encapsulation process including bonding and the removal of air bubbles with minimum thermal stress on the cells during the encapsulation process before the IEC tests (with maximum temperature at 85°C). The encapsulated devices were then stored in dry air (<1% RH in average) for 15 days to allow good bonding between the PIB and the glass, prior to environmental testing.

Test were performed to compare three types of devices:

Conventional (C) - Electrode element feedthrough through the encapsulation layer with use of PIB edge seal;

HBL feedthrough (NF) - PIB edge seal with TiO_2 feedthrough to FTO (this invention); and

No feedthrough fully sealed (FS) - full seal coverage of PIB encapsulation 114 and an electrical feedthrough in the TiO_2 layer 106 to extract carriers through a portion of the FTO 104a (this invention).

To study the effect of the key drivers (temperature and moisture) for PCE degradation of PIB encapsulated devices, accelerated testing of PIB encapsulated devices was performed in an environmental chamber according to IEC61215:2016 Damp Heat and Thermal Cycling tests, as

specified in the table below. The PCE of the devices were measured ex-situ in both scan directions ($J_{SC} \rightarrow V_{OC}$ and $V_{OC} \rightarrow J_{SC}$) at regular intervals.

Test	Conditions	Duration	Settlement time*
Damp Heat (DH)	85^0 C, 85% RH	Up to 1000 hours	2-4 hours
Thermal Cycling (TC)	-40^0 C to 85^0 C Dwell 15 minutes @ -40^0 C and 85^0 C	Up to 200 cycles	>1 hour
Humidity Freeze (HF)	-40^0 C to 85^0 C, 85% RH Dwell 30 minutes @ -40^0 C Dwell 20 hours @ 85^0 C, 85% RH Preconditioned by 50 TC	Up to 10 cycles	2-4 hours

The average PCE was calculated by averaging the PCE measured for opposite scans (see equation 1). The same method was used for other parameters such as V_{OC}, J_{SC}, FF and R_S. The hysteresis of PCE was quantified using equation 2. Note that cells free from hysteresis have Hysteresis Index = 1.

$$\text{Avg. PCE} = (\text{PCE } (V_{OC} \rightarrow J_{SC}) + \text{PCE } (J_{SC} \rightarrow V_{OC}))/2 \quad (1)$$

$$\text{H Index} = (\text{PCE } (J_{SC} \rightarrow V_{OC}))/(\text{PCE } (V_{OC} \rightarrow J_{SC})) \leq 1 \quad (2)$$

The "Mean" value was calculated by averaging the "Avg." parameters of multiple samples. The normalised Mean (with error bars) or Avg. (without error bars) parameters to their initial values for reporting in this work for ease of comparison.

To directly examine the effectiveness of PIB as a moisture barrier, a "Calcium Test" was performed which has been widely used to directly monitor moisture ingress in a sealed system. In the presence of moisture, thin layers of metallic calcium immediately become transparent signalling its reaction with water. To account for any moisture

possibly trapped in the as-fabricated PSC as well as moisture ingress from the external environment, PSCs were encapsulated with a cover glass that was centrally coated with a thermally evaporated thin (<100 nm) Ca layer for the accelerated tests: Damp Heat and Thermal Cycling. Photographs were taken before the test and at regular intervals during the test (ex-situ) to look for changes in the transparency and/or shape of the Ca films.

Test results obtained for (C) devices show degradation of PSCs during the accelerated testing as discussed above. NF devices with feedthrough through the electron transport layer in accordance with embodiments show a better stability. However, some degradation is shown that can be due to the loss of volatile products from the thermal stress.

The FS devices use a blanket PIB coverage and FTO feedthrough. This creates a pressure-tight environment which not only blocks the ingress of external moisture but also prevents the escape of any volatile materials from the PSC. When the moisture is eliminated and the pressure of the reaction system is maintained at a sufficient level, the decomposition and evaporation processes reaches equilibrium and further outgassing is inhibited.

Referring now to figures 4 and figure 5 there is shown a Damp Heat Test plot and Hysteresis Index for planar FS devices with $FAPbI_3$ absorber respectively. Figure 4 shows the normalised PCE against Damp Heat (bottom x-axis) and Thermal Cycling (top x-axis) tests. It is evident that the stability of the PSCs improves remarkably. All of the FS devices survived 540 hours of Damp Heat testing without degradation in their PCE. No degradation has shown in V_{OC},

J_{SC} and FF. This shows that, unlike EVA and UV-epoxy, long-term direct contact to PIB does not degrade the perovskite solar cells making it a suitable encapsulation material for PSC modules. With regards to the Thermal Cycling test, all FS devices passed the IEC61215:2016 standard by completing 200 thermal cycles without loss of PCE. In particular, RS improved during the course of the thermal cycling.

Referring now to figures 6 and 7 there is shown a Damp Heat Test plot and a Humidity Freeze Test plot for mesoporous FS devices with a $Cs_{0.05}FA_{0.80}MA_{0.15}PbI_{2.55}Br_{0.45}$ absorber. The results illustrate that over 1800 hours Damp Heat and 30 cycles Humidity Freeze tests, respectively, were survived.

The tables below summarise the results of accelerated tests on C-type devices; NF-type and FS-type. The results show the effectiveness of the complete encapsulation (FS) in maintaining a pressure-tight environment that stops volatile species from escaping, thereby preventing decomposition caused by thermal stress from the accelerated tests.

For the planar perovskite solar cell structure illustrated in Figure 1 the test results are summarised in the following table:

Test	Encapsulation	No. of samples	T_{80}	T_{50}
Damp Heat	C-type	2*	65 hr	200 hr
	NF-type	3	110 hr	300 hr
	FS-type	3	>540 hr	N/A
Thermal Cycling	C-type	2	35 cycles	54 cycles
	NF-type	4	75 cycles	>200 cycles
	FS-type	4	>200 cycles	N/A

For the mesoporous PSC structure illustrated in Figure 2 the test results are summarised in the following table:

Test	Encapsulation	No. of samples	Time
Damp Heat	FS-type	3	>1800 hr
Humidity Freeze	FS-type	2	>30 cycles

The photovoltaic devices manufactured in accordance with embodiments with FTO feedthroughs outperformed cells with other configurations. The complete PIB encapsulation showed improvements in PSC thermal stability. The Applicants are of the opinion that this is due to the suppressed escape of gaseous decomposition products and t-BP vapour, inhibiting the perovskite decomposition reaction and degradation of HTL. Unlike EVA or UV-cured epoxy, PIB was found to be inert to perovskite solar cell material. PIB has shown to have an easy application process, low application temperature and low cost. Planar cells that are PIB encapsulated using the method proposed herein survived 540 hours of IEC61215:2016 Damp Heat test and passed IEC61215:2016 Thermal Cycling test with no PCE degradation. To the best of the Applicants knowledge, these are the best accelerated lifetime test results published for c-TiO_2/$FAPbI_3$/PTAA based perovskite solar cells to date. Mesoporous cells that are polymer encapsulated using the method in accordance with embodiments of the present invention survived over 1800 hours of IEC61215:2016 Damp Heat test and over 30 cycles of IEC61215:2016 Humidity Freeze test. To the best of the Applicants knowledge, these are the best accelerated

lifetime test results to date published for mesoporous perovskite solar cells with MA content in the absorber layer.

Referring now to figure 8, there is shown a flow diagram with a series of steps that can be used to manufacture a photovoltaic device in accordance with embodiments.

A substrate comprising a transparent conductive oxide layer is provided at step 510 to form the device upon. In use, for this device configuration, the substrate is used as a superstrate, therefore incoming photons enter the device through the substrate.

At step 520, a first and a second portion of the transparent conductive oxide layer are formed by creating an opening in the transparent conductive oxide layer. The opening may be formed using a laser. Further, at step 530, an electron transport layer, or electron transport layer, is formed onto the transparent conductive oxide layer.

At this state, the perovskite-based light-absorbing layer is formed on at least a portion of the electron transport layer, step 540, and a hole transport layer is then formed onto the light absorbing layer, step 550.

At step 560, an electrode element is formed onto the hole transport layer so that the electrode element is in electrical contact with the hole transport layer and with the second portion of the transparent conductive oxide layer. To form a connection between the electrode element and the second portion of the transparent conductive oxide layer, at least one opening is formed in the electron transport layer. The opening may be formed using a laser, chemical etching or a physical etching method.

At step 570, an encapsulation layer is formed at the rear of the device. The encapsulation layer wraps around a structure comprising the light-absorbing layer, the hole transport layer and the electrode element and is in continuous contact with the electron transport layer along the entire perimeter of the structure.

The transparent conductive oxide layer, the electron transport layer, the hole transport layer and the electrode element are such that, in use, electrons generated in the light absorbing layer travel through the electron transport layer to the first portion of the transparent conductive oxide layer before being extracted from the device; and holes generated in the light absorbing layer travel through the hole transport layer to the electrode element and from the electrode element to a second portion of the transparent conductive oxide layer before being extracted from the device.

The devices and methodologies described herein relate to perovskite based photovoltaic devices. However, it will be appreciated by persons skilled in the art, that the electrode feedthrough design and the full seal encapsulation at the core of this invention may be applied to different types of thin-film photovoltaic devices. In particular, the invention may be applied without substantial modification to perovskite cells that are inverted in respect to the device described herein. In other words, where the electron transport layer and the hole transport layer are inverted.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without

departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

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The Claims Defining the Invention are as Follows:

1. A photovoltaic device comprising:

a substrate;

a transparent conductive oxide layer in contact with the substrate;

an electron transport layer in contact with the transparent conductive oxide layer;

a light-absorbing layer comprising a material with a perovskite structure; the light absorbing material being in contact with the electron transport layer;

a hole transport layer in contact with the light absorbing layer such that the light absorbing layer is positioned between the electron transport layer the hole transport layer;

an electrode element in electrical contact with the hole transport layer; and

an encapsulation layer disposed at the rear of the device; the encapsulation layer being arranged to wrap around a structure comprising the light-absorbing layer, the hole transport layer and the electrode element and to be in continuous contact with the electron transport layer along the entire perimeter of the structure;

wherein the transparent conductive oxide layer, the electron transport layer, the hole transport layer and the electrode element are arranged such that, in use, electrons generated in the light absorbing layer travel through the electron transport layer to a first portion of

the transparent conductive oxide layer before being extracted from the device; and holes generated in the light absorbing layer travel through the hole transport layer to the electrode element and from the electrode element to a second portion of the transparent conductive oxide layer before being extracted from the device.

2. The photovoltaic device of claim 1, wherein the photovoltaic device is a planar device.

3. The photovoltaic device of claim 1, wherein the photovoltaic device is a mesoporous device.

4. The device of any one of the preceding claims, wherein the first and second portion of the transparent conductive oxide are electrically insulated from each other.

5. The device of any one of the preceding claims, wherein the electron transport layer comprises one or more openings arranged to enable electrical contact between the electrode element and the second portion of the transparent conductive oxide.

6. The device of any one of claims 1 to 4, wherein the electron transport layer does not have physical openings, however, its thickness is such that holes are able to tunnel from the electrode element to the second portion of the transparent conductive oxide.

7. The device of any one of the preceding claims, wherein the encapsulation material is such to form a pressurised seal around the structure comprising the light-absorbing layer, the hole transport layer and the electrode element allowing to substantially reduce the velocity of chemical

reactions in the structure while the photovoltaic device is in use.

8. The device of claim 7, wherein the continuous seal formed by the encapsulation layer allows to prevent oxygen or moisture from entering into contact with the structure and be detrimental to active parts of the device.

9. The device of claim 7 or claim 8, wherein the encapsulation material comprises a suitable material that has the following properties: water permeation rate below 0.1 g*mm/m^2*day at 23 °C, 100% R.H., air permeation rate below 1000 cm^3*mm/m^2*day*atm at 80 °C, resistivity larger than 10^{10} ohm*cm at 23 °C, chemically inert to perovskite photovoltaic device and good adhesion to the hole blocking layer or transparent conductive oxide layer.

10. The device of any one of the preceding claims wherein the encapsulation material comprises a polymeric material.

11. The device of claim 10 wherein the encapsulation material comprises at least one of PIB and PO.

12. The device of any one of the preceding claims wherein the electron transport layer comprises TiO_2.

13. The device of any one of the preceding claims, wherein the hole transport layer comprises PTAA.

14. The device of any one of the preceding claims, wherein the electrode element is made by gold.

15. The device of any one of the preceding claims, wherein the device further comprises a glass cover arranged at the rear of the device.

16. A method of forming a photovoltaic device; the method comprising the steps of:

providing a substrate comprising a transparent conductive oxide layer;

forming a first and a second portion of the transparent conductive oxide layer by creating an opening in the transparent conductive oxide layer;

forming an electron transport layer onto the transparent conductive oxide layer;

forming a light-absorbing layer onto the electron transport layer; the light-absorbing layer comprising a material with a perovskite structure;

forming a hole transport layer onto the light absorbing layer;

forming an electrode element onto the hole transport layer in a manner such that the electrode element is in electrical contact with the hole transport layer and with the second portion of the transparent conductive oxide layer; and

forming an encapsulation layer at the rear of the device in a manner such that the encapsulation layer wraps around a structure comprising the light-absorbing layer, the hole transport layer and the electrode element and to be in continuous contact with the electron transport layer along the entire perimeter of the structure;

wherein the transparent conductive oxide layer, the electron transport layer, the hole transport layer and the electrode element are such that, in use, electrons

generated in the light absorbing layer travel through the electron transport layer to the first portion of the transparent conductive oxide layer before being extracted from the device; and holes generated in the light absorbing layer travel through the hole transport layer to the electrode element and from the electrode element to a second portion of the transparent conductive oxide layer before being extracted from the device.

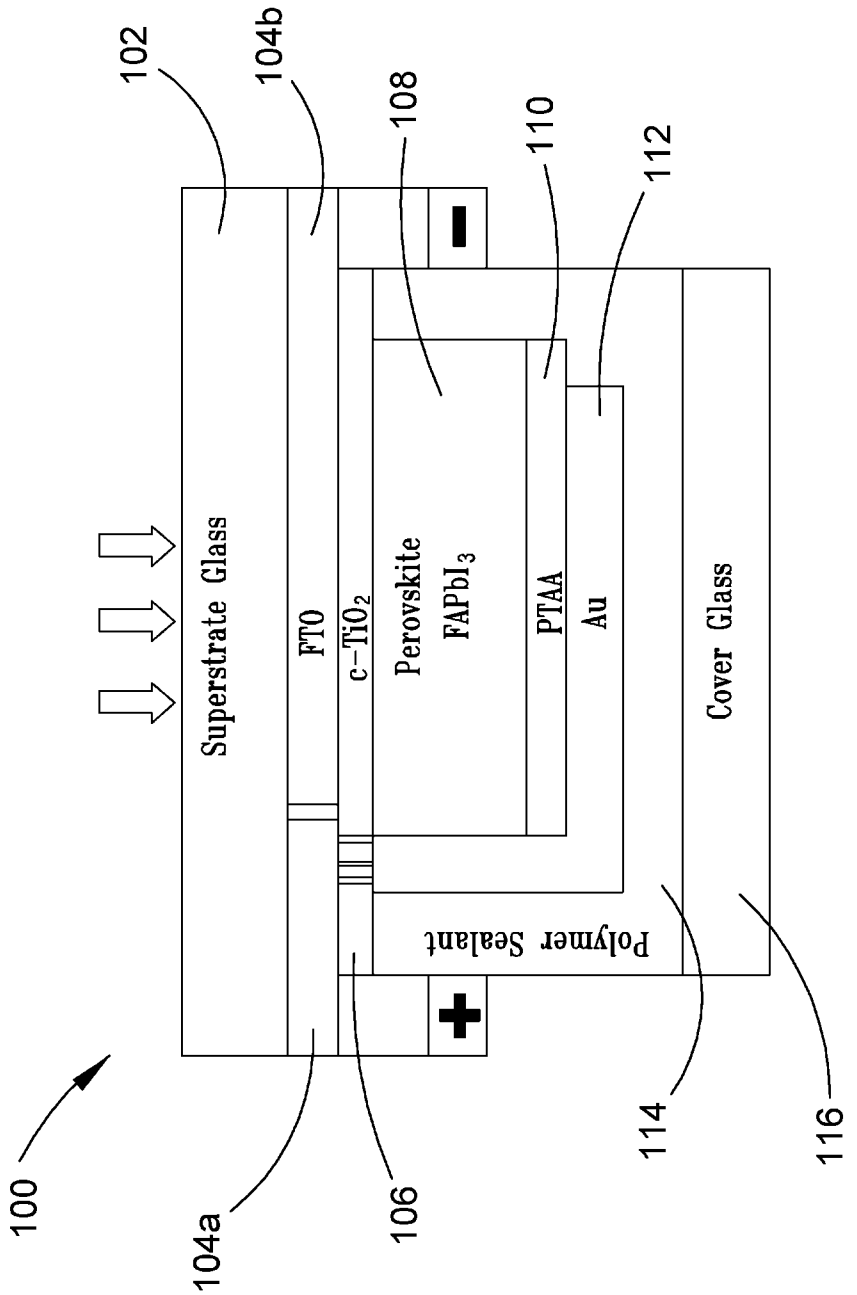
17. The method of claim 16, wherein the photovoltaic device is a planar device.

18. The method of claim 16, wherein the photovoltaic device is a mesoporous device.

19. The method of any one of claims 16 to 18, wherein the method further comprises the step of forming one or more opening in the electron transport layer to facilitate electrical contact of the electrode element with the second portion of the transparent conductive oxide.

20. The device of any one of claims 16 to 19 wherein the encapsulation material comprises a polymeric material.

21. The device of any one of claims 16 to 20 wherein the encapsulation material comprises at least one of PIB and PO.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104b
108
110
112
Superstrate Glass
FTO
c-TiO2
Perovskite
FAPbI3
PTAA
Au
Cover Glass
Polymer Sealant
100
104a
106
114
116

FIGURE 1

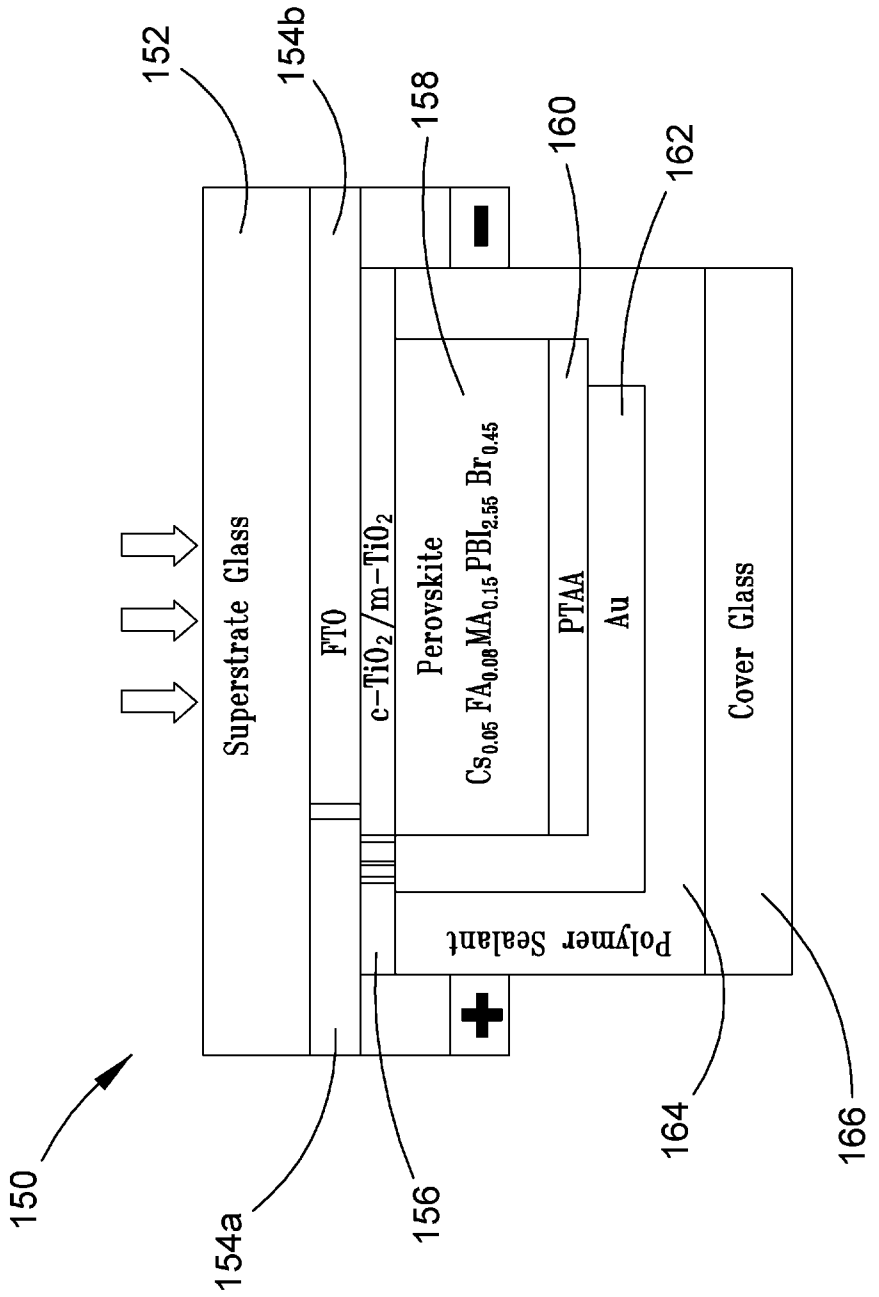

152
154b
158
160
162
Superstrate Glass
FTO
c-TiO2/m-TiO2
Perovskite
Cs0.05 FA0.08 MA0.15 PBI2.55 Br0.45
PTAA
Au
Cover Glass
Polymer Sealant
150
154a
156
164
166

FIGURE 2

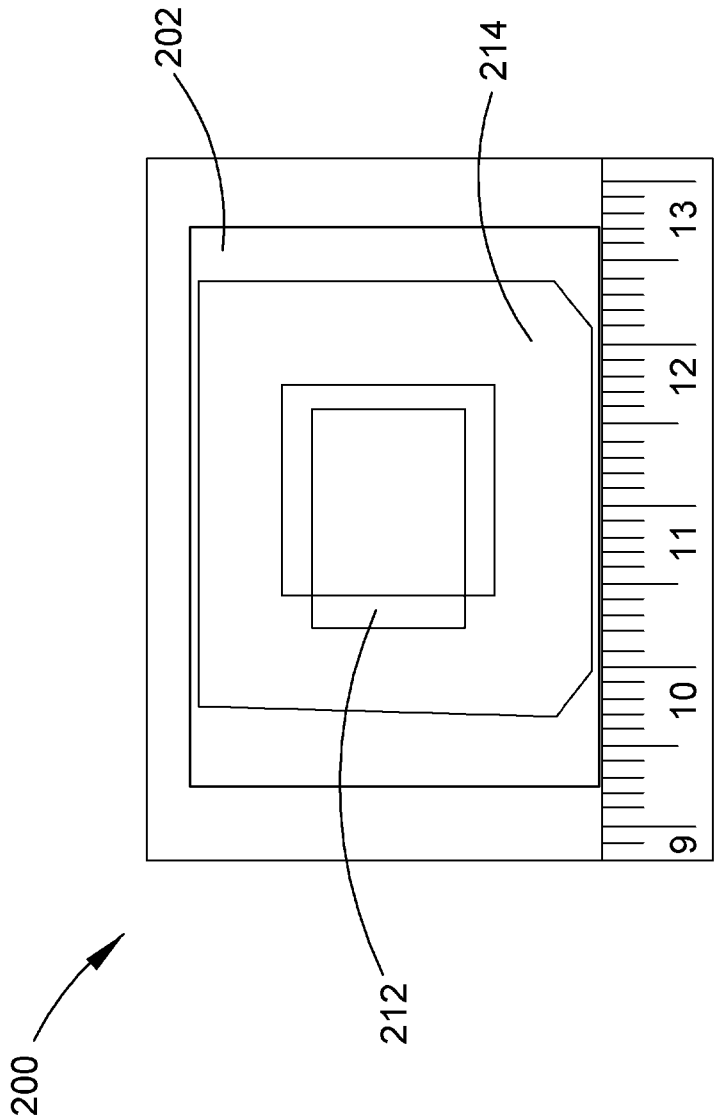


FIGURE 3

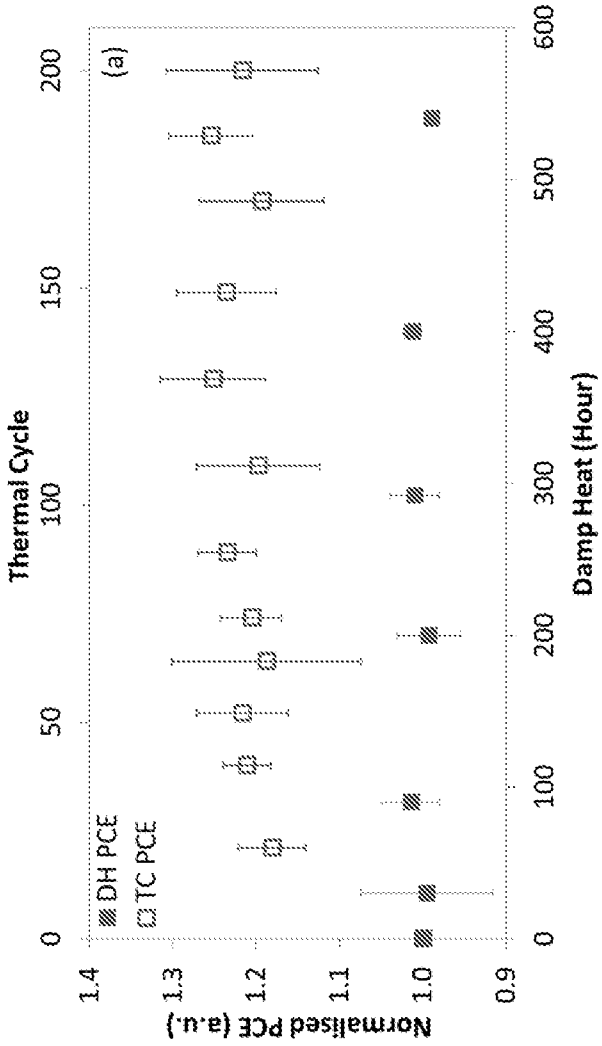
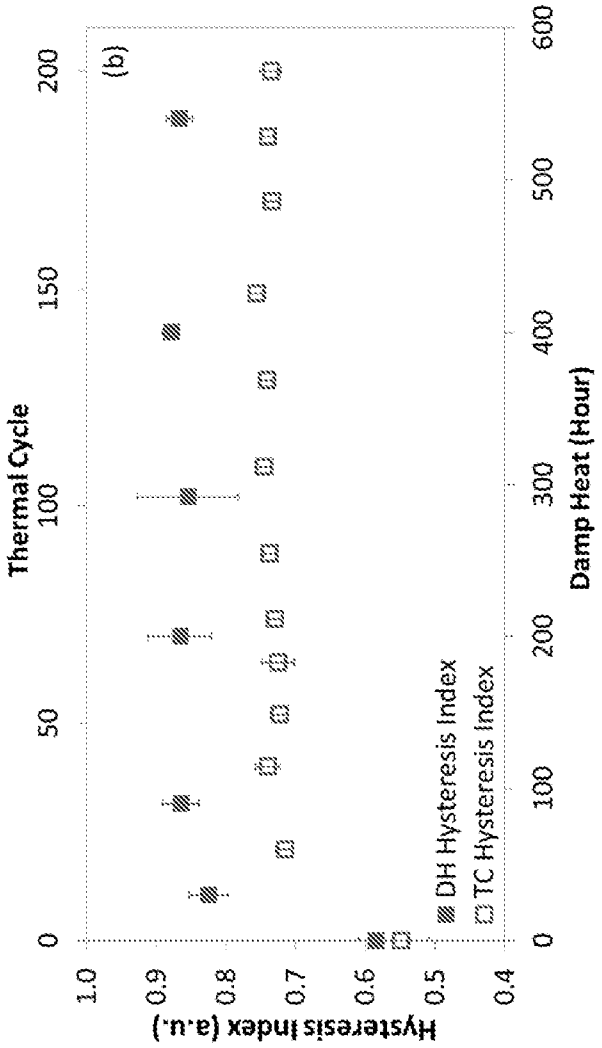

(a)
DH PCE
TC PCE
Thermal Cycle
Damp Heat (Hour)
Normalised PCE (a.u.)
0
50
100
150
200
0
100
200
300
400
500
600
1.4
1.3
1.2
1.1
1.0
0.9

FIGURE 4


(b)
Thermal Cycle
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50
100
150
200
Damp Heat (Hour)
0
100
200
300
400
500
600
Hysteresis Index (a.u.)
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0.9
0.8
0.7
0.6
0.5
0.4
DH Hysteresis Index
TC Hysteresis Index

FIGURE 5

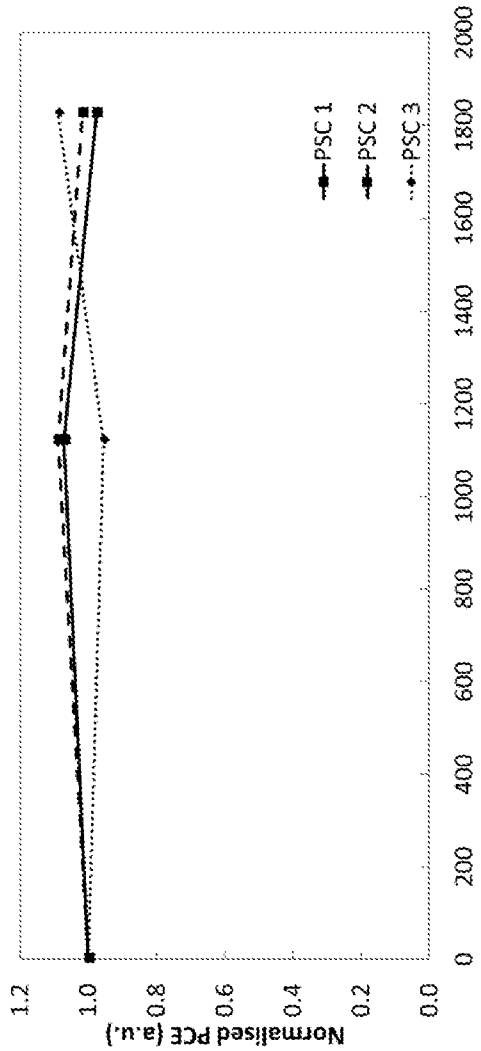
Normalised PCE (a.u.)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Damp Heat Hour
PSC 1
PSC 2
PSC 3

FIGURE 6

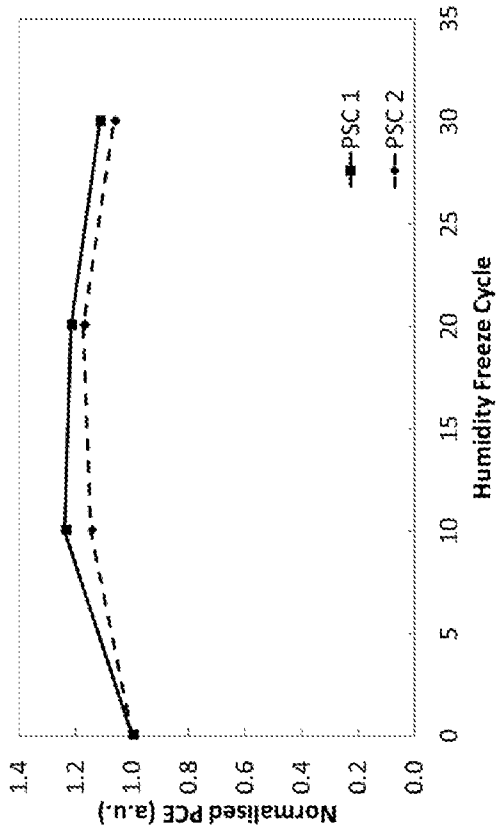
Normalised PCE (a.u.)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
35
Humidity Freeze Cycle
PSC 1
PSC 2

FIGURE 7

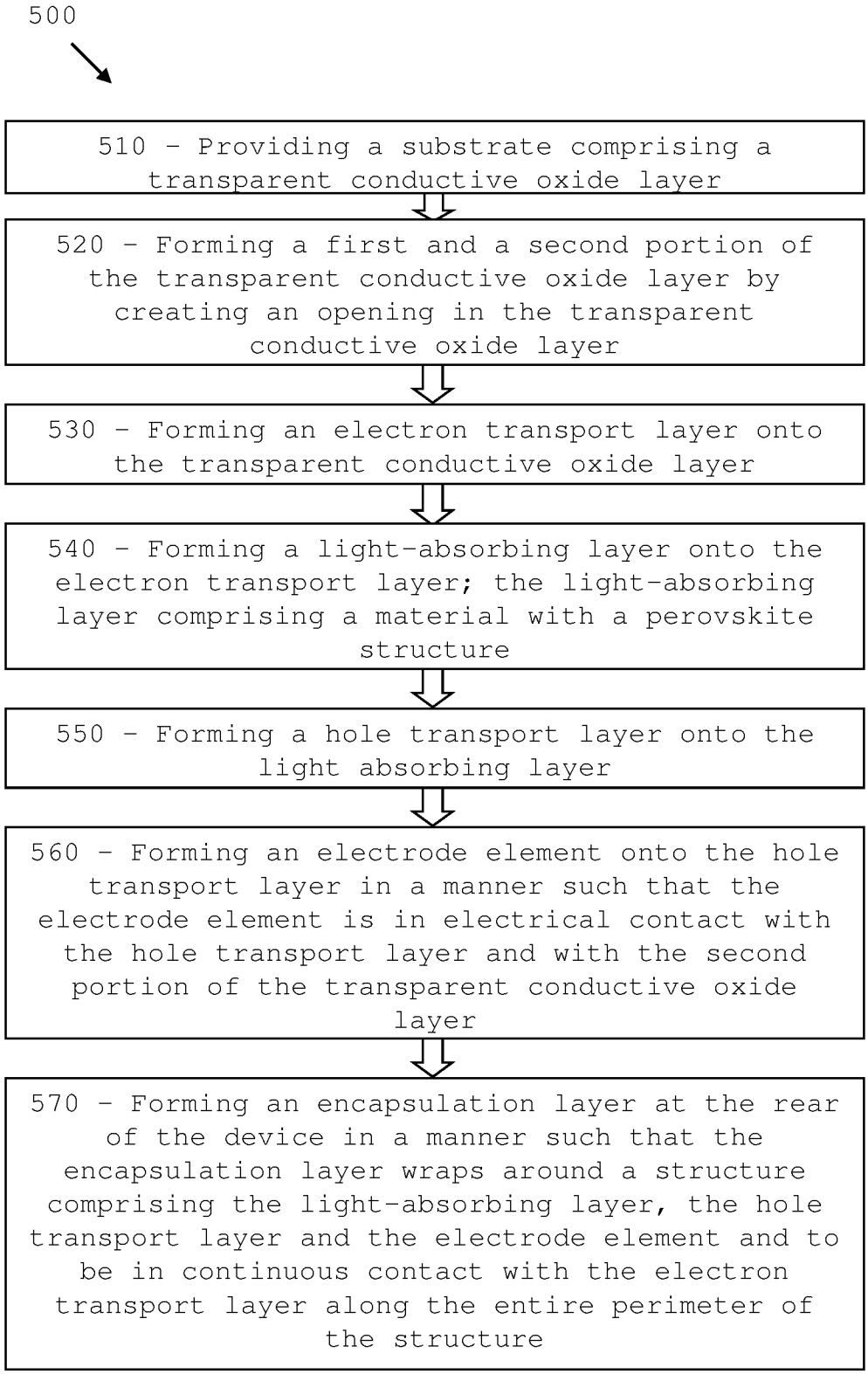
500
510 – Providing a substrate comprising a transparent conductive oxide layer
520 – Forming a first and a second portion of the transparent conductive oxide layer by creating an opening in the transparent conductive oxide layer
530 – Forming an electron transport layer onto the transparent conductive oxide layer
540 – Forming a light-absorbing layer onto the electron transport layer; the light-absorbing layer comprising a material with a perovskite structure
550 – Forming a hole transport layer onto the light absorbing layer
560 – Forming an electrode element onto the hole transport layer in a manner such that the electrode element is in electrical contact with the hole transport layer and with the second portion of the transparent conductive oxide layer
570 – Forming an encapsulation layer at the rear of the device in a manner such that the encapsulation layer wraps around a structure comprising the light-absorbing layer, the hole transport layer and the electrode element and to be in continuous contact with the electron transport layer along the entire perimeter of the structure

FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2018/050694

A. CLASSIFICATION OF SUBJECT MATTER

H01L 31/048 (2014.01) H01L 51/42 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases: PATENW in Logical databases (WPIAP, EPODOC, Full text), IPC/CPC marks: H01L31/04, H01L27/142, Y02E10/50 and keywords: photovoltaic, PV, solar cell, photoelectric, solar batteries, encapsulation, cap, laminate, shield, cover, protect, seal, wrap, hermetic, electrode, pad, contact, conducting, metal, ITO, FTO, TCO, moisture, humidity, water, high temperature, degrade, detrimental, hole transporting layer, p type, electron transporting layer, n type, halide, perovskite and similar terms. Applicant(s)/Inventor(s) name search in Espacenet, AusPat and Google Patents/Google scholar/Google: Applicant(s)/Inventor(s) name search in Espacenet, AusPat and Google Patents/Google scholar/Google: Applicant name: NEWSOUTH INNOVATIONS PTY LIMITED; Inventors name: Shi, Lei; Young, Trevor Lindsay and keywords: solar cell, photovoltaic cell, encapsulation, moisture, high temperature, perovskite and similar terms. Applicant(s)/Inventor(s) name searched in internal databases provided by IP Australia.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 September 2018	14 September 2018
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Jayati Ray AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262223654

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Dong Q. et al., "Encapsulation of Perovskite Solar Cells for High Humidity Conditions", ChemSusChem, ChemPubSoc, Europe, 9th August 2016, vol. 9, no.18, pages 2597–2603. Fig. 1, Results and discussion part, Experimental Section	1-21
X	Han Y. et al., "Degradation observations of encapsulated planar CH3NH3PbI3 perovskite solar cells at high temperatures and humidity", Journal of Materials Chemistry A, volume 3, no.15, 2015, page 8139 - 8147. Figs. 1-2, Experimental part	1-21
X	JP 2016178288 A (RICOH CO LTD) 06 October 2016 & US2017243698 A1, used for English translation Figs. 1A-1C, paragraphs 0250-0253	1-21

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2018/050694**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
JP 2016178288 A	06 October 2016	JP 2016178288 A	06 Oct 2016
		US 2017243698 A1	24 Aug 2017

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.