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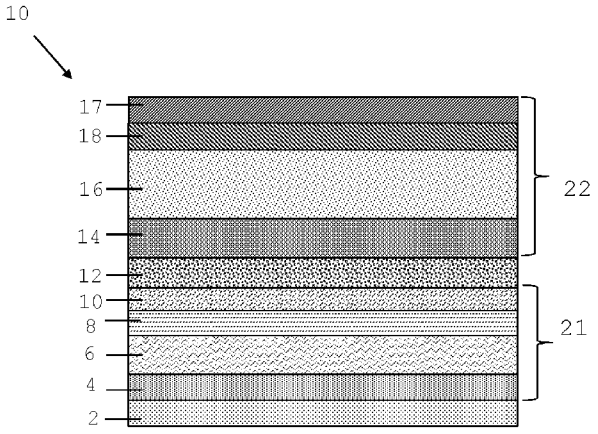

FIGURE 1

(57) Abstract: The present disclosure is directed to a photovoltaic device comprising: a photon receiving surface; a first photon absorbing layer comprising a material that has a perovskite structure and having a first bandgap; and a second photon absorbing layer comprising an inorganic material that has a chalcogenide structure and having a second bandgap; the first photon absorbing layer being positioned at least partially between the photon receiving surface and the second photon absorbing layer. The second photon absorbing layer is arranged to provide encapsulation for at least a portion of the first photon absorbing layer and the photovoltaic device is arranged such that received photons are absorbed by at least one ofthe first and the second photon absorbing layers. In embodiments the perovskite structure is methylammonium lead bromide ($CH_3NH_3PbBr_3$) and the chalcogenide structure is antimony selenide (Sb_2Se_3).

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A PHOTOVOLTAIC CELL AND A METHOD OF FORMING A PHOTOVOLTAIC CELL

Field of the Invention

The present invention generally relates to photovoltaic thin film devices comprising a Perovskite based light absorbing material.

Background of the Invention

The majority of commercial photovoltaic (PV) modules based on silicon solar cells utilise solar cells fabricated using high quality silicon wafer. Despite the constant drop of silicon prices over the last few years, the cost of silicon still represents a large portion of the final price of these photovoltaic modules.

Substantial investments have been made in the last 10 years to develop photovoltaic devices which use inexpensive materials, possibly in very small quantities. These photovoltaic devices are often referred to as thin film solar cells. Cadmium telluride cells are an example of a thin film solar cell technology which had a major commercial success and competes on the market with conventional wafer-based silicon cells.

Recently, PV devices that use perovskite based light absorbing materials have shown very good performance with a low production cost. A record efficiency of 22% has been demonstrated for a perovskite based solar cell in late 2016. Moreover, perovskite PVs has the lowest energy

payback time (EPBT) compared to any PV technology ever developed.

One of the main problems of perovskite based PV devices is related to operational stability. In other words, the time it takes before the performance of the PV device start degrading. The stability of current perovskite PV devices is in the range of 4000 hours. This figure is not compatible with the majority of commercial PV applications.

There is a need in the art for perovskite based PV devices with improved energy conversion efficiency and longer term stability.

Summary of the Invention

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

a photon receiving surface;

a first photon absorbing layer comprising a material that has a Perovskite structure and having a first bandgap; and

a second photon absorbing layer comprising an inorganic material that has a Chalcogenide structure and having a second bandgap; the first photon absorbing layer being positioned at least partially between the photon receiving surface and the second photon absorbing layer;

wherein the second photon absorbing layer is arranged to provide encapsulation for at least a portion of the first photon absorbing layer and the photovoltaic

device is arranged such that received photons are absorbed by at least one of the first and the second photon absorbing layers.

In advantageous embodiments the second photon absorbing layer is arranged to provide complete high quality encapsulation of the photovoltaic device and no further encapsulation is required.

In embodiments, the first photon absorbing layer comprises a Methylammonium Lead Bromide ($CH_3NH_3PbBr_3$) Perovskite and the second photon absorbing layer comprises antimony selenide (Sb_2Se_3). The thickness of the Sb_2Se_3 may be between 200nm and 1µm.

In embodiments, the device allows for an energy conversion efficiency that is at least 8% relative higher than the efficiency of a corresponding device with a single Perovskite absorbing. Further, the device may provide an improved resilience to degradation. For example, degradation of the efficiency figure may be lower than 2% for a period of at least 60 days.

In embodiments, the second photon absorbing layer is arranged to reduce the amount of moisture reaching the first photon absorbing layer by 50% relative when compared to a Perovskite photovoltaic device with a single photon absorbing layer similar to the first photon absorbing layer. The second photon absorbing layer may be arranged to reduce the amount of moisture reaching the first photon absorbing layer by 95% when compared to a Perovskite photovoltaic device with a single photon absorbing layer similar to the first photon absorbing layer.

In some embodiments, the device further comprises a silver or gold interconnecting layer with a thickness comprised between 2nm and 5nm disposed between the first and the second photon absorbing layers. The interconnecting layer may be arranged to reflect a portion of high energy photons, that have entered the device, towards the second photon absorbing layer.

In some embodiments, the device further comprises a wide bandgap n-type metal oxide layer comprising TiO_2 or ZnO nanoparticles disposed between the photon receiving surface and the first photon absorbing layer; the layer being arranged as an electron transport layer which facilitates the transport of electrons from the photovoltaic device to a contact structure. In addition, the device may comprise a WO_3 layer, disposed between the second photon absorbing layer and a rear contact of the photovoltaic device, arranged as an hole transport layer which facilitates the transport of holes from the photovoltaic device to a contact structure.

In embodiments, the first bandgap is larger than the second bandgap and the Perovskite material is a self-assembled material comprising an inorganic-organic compound.

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

forming a first solar cell structure on a substrate, the first solar cell structure comprising a first photon absorbing layer that comprises a material

that has a Perovskite structure and having a first bandgap; and

forming a second solar cell structure comprising a second photon absorbing layer comprising an inorganic material that has a Chalcogenide structure and having a second bandgap; the second solar cell being positioned at least partially onto the first solar cell;

wherein the second solar cell is in electrical contact with the first solar cell and is arranged to provide encapsulation of at least a portion of the first solar cell; and the photovoltaic device is arranged such that received photons are absorbed by at least one of the first and the second solar cells.

In embodiments, the method further comprises the step of depositing a silver or gold interconnecting layer between the steps of forming the first and the second solar cells. The interconnecting layer has a thickness comprised between 2nm and 5nm and is arranged to reflect a portion of high energy photons that have entered the device towards the second photon absorbing layer.

The method may further comprise the step of selecting at least one property of the silver or gold layer to tune the optical field distribution within the photovoltaic device. The electrical contact of the gold or silver interconnection layer can be further increased by introducing a thin layer (10-20nm) of water-free Pedot:PSS/C_{60} interlayers.

In some embodiments, the method comprises the step of evaporating Sb_2Se_3 at a vacuum pressure between 6 and 10

mTorr from a Sb_2Se_3 powder source or spin coating a solution containing Sb_2Se_3.

Further, the method may comprise the step of forming a layer comprising TiO_2 or ZnO nanoparticles disposed between the photon receiving surface and the first photon absorbing layer; the layer being arranged as an electron transport layer which facilitates the transport of electrons from the photovoltaic device to a contact structure. In addition, WO_3 layer may be formed between the second photon absorbing layer and a rear contact of the photovoltaic device; the WO_3 layer comprising WO_3 being arranged as an hole transport layer which facilitates the transport of holes from the photovoltaic device to a contact structure.

The encapsulation of perovskite based PV devices consists of a protective layer, disposed onto the exposed surface of the device, that protects the device from the external environment, in particular from moisture, to prevent degradation of the perovskites. The encapsulation layers can just be disposed onto the portion exposed to the environment and may not cover the back surface or sides of the devices. Encapsulation techniques based composite carbon nanotubes and an inert polymer matrixes have been used in the art, but did not achieve long term good performance.

Advantageous embodiments of the invention use an antimony selenide (Sb_2Se_3) photon absorbing layer in conjunction with an organic-inorganic perovskite photon absorbing layer in a tandem structure. This allows improving the energy conversion efficiency of the PV devices while

providing high quality encapsulation and therefore improving stability.

Antimony selenide exhibits suitable optoelectronic properties — it has an acceptable bandgap of 1.1 eV and strong absorption (≥ 105 cm^{-1}) — and can be deposited by thermal evaporation at low temperature (350 °C) and under low vacuum (~8 mTorr).

Furthermore, antimony selenide, as used in these embodiments, provides high quality encapsulation for the PV device and no further encapsulation is required.

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 is a schematic illustration of a cross-section of a photovoltaic device comprising of two solar cell structures, in accordance with an embodiment;

Figure 2 is an energy band representation of the photovoltaic device, in accordance with an embodiment;

Figure 3 is a schematic illustration of the optical field distribution in the photovoltaic device of figure 1;

Figure 4 shows SEM micrographs of Sb_2Se_3 thin films used to encapsulate devices in accordance with embodiments;

Figure 5 shows 2D and 3D AFM images of Sb_2Se_3 thin films used to encapsulate devices in accordance with embodiments;

Figure 6 shows the I-V curve of a single junction Sb_2Se_3 solar cell fabricated with 300°C annealed films (a) and the I-V curve of a single junction wide band gap perovskite ($FAPbI_3$-$MAPbBr_3$) solar cell (b).

Figure 7 shows simulated current-voltage curves for a Chalcogenide solar cell, a Perovskite solar cell, and the Chalcogenide-Perovskite tandem device of figure 1;

Figure 8 shows efficiency-lifetime curves for a conventional Perovskite device and the Chalcogenide-Perovskite tandem device of figure 1; and

Figure 9 is a flow-diagram outlining a series of method steps for manufacturing a photovoltaic device comprising of two photon absorbing layers of different materials, in accordance with an embodiment.

Detailed Description of Embodiments

Embodiments described herein are directed to a photovoltaic device which has photon receiving surface, a first photon absorbing layer comprising a material that has a Perovskite with a first bandgap; and a second photon absorbing layer comprising an inorganic material that has a Chalcogenide structure with a second bandgap. The PV device is configured as a tandem cell and the second photon absorbing layer provides encapsulation of the device while, at the same time, absorbing photons and contributing to the generation of the device photo-current.

The perovskite photon absorbing layer is positioned between a glass substrate and the Chalcogenide photon absorbing layer. The perovskite photon absorbing layer

receives photons, through the transparent substrate, before the Chalcogenide photon absorbing layer. Photons not absorbed by the perovskite layer can be absorbed by the Chalcogenide layer. This device design provides improved power conversion efficiency (PCE) and stability of the device.

A contribution to the improved PCE is provided by the increased open circuit voltage (VOC) of the photovoltaic device. Another contribution to the improved PCE is provided by the increased photocurrent due to better absorption of the solar spectrum over the first and the second absorbing layers.

In the embodiment described, a Methylammonium Lead Bromide ($CH_3NH_3PbBr_3$) is used to form the first photon absorbing layer. $CH_3NH_3PbBr_3$ has a perovskite structures and is deposited by spin-coating. The low energy and ease of deposition provides a substantial advantage in the manufacturing process of the photovoltaic device.

Referring to figure 1, there is shown a schematic representation of a cross-section of a photovoltaic device 10 realised on a glass substrate 2. The glass substrate 2 2 is coated with a conductive transparent oxide (TCO), such as ITO. Device 10 further comprises a first photon absorbing layer 6 comprising of a material that has Perovskite structure and a second photon absorbing layer 16 comprising of an inorganic material that has a Chalcogenide structure.

The Perovskite layer 6 is made of Methylammonium Lead Bromide ($CH_3NH_3PbBr_3$) material which is a p-type semiconducting material. The $CH_3NH_3PbBr_3$ layer has a direct

band gap of 1.93 to 2.3 eV that corresponds to a light absorption onset of less than or equal to 550 nm. This makes this material an excellent light harvester with significantly improved stability in humid atmosphere.

The Chalcogenide layer 16 is made of Antimony Selenide (Sb_2Se_3), which is a simple binary compound with a fixed phase and stoichiometry. The thickness of the Sb_2Se_3 layer 16 is approximately 200 nm to 1 µm. It has a very strong absorption coefficient (>105 cm^{-1} at short wavelengths) and its bandgap is approximately 1.1 eV. The constituent of Sb_2Se_3 is non-toxic and low in cost. The Sb_2Se_3 material can be deposited by thermal evaporation at a vacuum pressure between 6 and 10 mTorr from a Sb_2Se_3 powder source or by spin coating a solution containing Sb_2Se_3.

Chalcogenide layer 16 is disposed above the Perovskite layer 6 in device 10 and works as an encapsulation layer to improve the lifetime of the unstable Perovskite material. Therefore, device 10 exhibits an improved stability in comparison to a PV device comprising a single photon absorbing layer of Perovskite material.

In addition to this, Chalcogenide layer 16 has a different range of absorption spectrum in comparison to the Perovskite absorption spectrum. Therefore, tandem device 10 absorbs photons from a wider spectrum of wavelengths. Device 10 allows absorbing a broader range of wavelengths of solar spectrum to develop high efficiency and stable thin film PV devices. In the embodiment described, the photovoltaic device comprises further layers as illustrated in figure 1. These layers are arranged in a way to form two separate solar cell structures; a front solar cell 21 (comprising Perovskite layer 6) and a back

solar cell 22 (comprising Chalcogenide layer 16). The front solar cell 21 is disposed on the glass substrate 2. A wide bandgap n-type metal oxide layer 4 is disposed between the photon receiving surface 2 and the Perovskite layer 6. This layer comprises either TiO_2 or ZnO nanoparticles. Metal oxide layer 4 is an electron transport layer that facilitates the transport of electrons from the photovoltaic device 10 to a contact electrode 3. An electron barrier layer 8, comprising MoO_3, is placed on top of the Perovskite layer 6. A semi-transference silver (Ag) layer 10 is deposited on MoO_3 layer 8. Silver layer 10 establishes a series connection between the front solar cell 21 and back solar call 22. The Ag layer 10 also helps in reflecting back a portion of high energy photons leaking out of the Perovskite layer 6 without getting absorbed. This layer has a thickness of approximately 2 nm to 5 nm. In alternative embodiments, this layer 6 can be replaced by a thin gold layer. One or more properties (such as thickness) of the silver or gold layers can be modified to tune the optical field distribution within the photovoltaic device.

PFN layer 12 is added adjacent to the gold or silver interconnection layer which functions as a dipole layer reducing the work function of the metal interconnection layer to facilitate the charge recombination enabling efficient electrical contact between the top and bottom cells.

The back cell 22 comprises an electron transport layer 14 to facilitate the transport of electrons from the back cell 22 to the front cell 21. The electron transport layer is realised using a metal oxide such as ZnO or TiO_3. The metal oxide layer 14 is disposed between the PFN layer 12

and the Chalcogenide layer 16. A hole transport layer 18 is disposed between the Chalcogenide layer 16 and a rear metal contacting structure 17 which is made of silver (Ag). Hole transport layer 18 comprises WO_3 and facilitates the transport of holes from the PV device to the metal contacting structure 17.

The metallic contacting structure 17, comprises of a pattern of silver contacts or a planar silver layer, is in electrical contact with the front solar cell and is arranged to extract electrons from the photovoltaic device 10.

Incoming light photons reach the glass substrate 2 and get transmitted to the metal oxide layer 4 of the front solar cell 21. A portion of these photons is absorbed by the Perovskite layer 6 and converted in electron-hole pairs in the front solar cell 21. The majority of the photons absorbed by the Perovskite material have an energy which is higher than the bandgap of the Perovskite layer 6. A further portion of photons, generally with energy lower than the bandgap of Perovskite layer 6, is transmitted through the front solar cell to the back solar cell. A portion of these transmitted photons is absorbed in the Chalcogenide layer 16 and converted to electron-hole pairs in the back solar cell 22. The majority of these photons, converted in the second solar cell, have an energy which is higher than the bandgap of Chalcogenide layer 16. The Perovskite layer 6 absorbs high energy photons from the solar spectrum and the Chalcogenide layer 16 absorbs the transmitted low energy photons. This is because the band gap of Perovskite material is larger than the band gap of Chalcogenide material.

Photons having an energy smaller than the band gap of the Perovskite layer 6 and the Chalcogenide layer 16 may be transmitted through both the front and the back solar cells.

In order to further avoid degradation of the Perovskite light absorbing material, in some embodiments, perovskite layer 6 may be infiltrated in a 2D and 3D mix-structure. For example, a scaffold oxide, such as a ZrO2 structure, may be formed and the Perovskite material may be infiltrated in such structure to improve stability.

The mixture of 2D/3D perovskite structure forms an exceptional gradually-organized multi-dimensional interface. The interface engineering a built-in 2D/3D perovskite will form a peculiar bottom-up phase-segregated graded structure. The unique combination of the 2D layer acting as a protective window against moisture, preserving the 3D perovskite and of the efficient 3D one provides the stable perovskite solar cells for widespread deployment.

Referring now to figure 2, there is shown an energy band diagram 20 of device 10. Reference alphabets 'c' and 'v' in this figure are used to refer to conduction and valance band edges of the layers of the device 10. Energy levels in figure 2 are referred to the vacuum level. Referring to the front cell in figure 2, it is evident that the conduction band edge 6c of the Perovskite material is higher in energy than the conduction bands of TiO_2 (4c) and ITO (2c) layers. This configuration of the conduction band edges allows electrons to flow towards the glass substrate 2 of the front cell. Electrons generated in the front solar cell 21 are prevented from travelling towards the back solar cell 22 due to very high conduction band edges

(not shown in figure 2) of the MoO_3 layer. The valence band edge 6v is lies between the valence band edges of the TiO_2 layer, 4v, and the MoO_3 layer, 8v. This configuration of the valence band edges allows holes to flow towards the dipole layer 12 and recombine with electrons coming from the back solar cell 22. Holes generated in the front solar cell 21 are prevented from travelling towards the glass substrate 2.

The energy bands of the second solar cell in figure 2 show the same trend as discussed with reference to the first solar cell. WO_3 layer 18 has a high energy conduction band edge (not shown in figure 2) that prevents electrons from reaching the Ag contact 17. The valence band edge 14v prevents holes from reaching the dipole layer 12. Electrons generated in the back cell 22 recombine with holes coming from the front solar cell 21 in the dipole layer 12. Holes generated in the back solar cell 22 can be extracted through the Ag contact 17.

The interfacial dipole layer reduces the work function of the metal (Gold or silver) interconnection layer, facilitating better charge recombination across the interface, thereby enabling efficient electrical contact between the top and bottom cells.

Figure 3 is a schematic illustration of the optical field distribution for the front (reference numeral 31) and back (reference numeral 33) cells having an ultra-thin inter-connection Ag layer (reference numeral 32) in-between. The sun-light incidenting on the photon receiving surface of the device comprises of a wide range of photons with different energies. Each active layer of device is responsible for absorbing certain intensities and

wavelengths of light from visible to near infrared wavelengths of the solar spectrum. The front cell 31 absorbs high energy photons whereas the low energy photons are transmitted through the front cell 31 and they get absorbed at the back cell 33. Most of the high energy photons leaking out of the front cell 31 and moving towards the back cell 33 are reflected back to the front cell by the intermediate semi-transference Ag layer 32. As a result a micro-cavity is formed in the back cell 33 providing an effective optical manipulation between the front and back cells. The reflectivity of the ultra-thin Ag layer 32 can manipulate the optical field distribution within the front and the back cells.

Figure 4 shows SEM micrographs of the Sb_2Se_3 thin films:(a) as deposited with substrate heating; (b) annealed at 100˚C; (c) annealed at 200˚C; and (d) annealed at 300˚C.

The as-deposited and annealed films have shown almost similar topography with roughness values falling between the ranges of 13.8 nm to 18 nm. All the films have showed smoother and tightly packed morphology. The roughness values are reduced slightly after the annealing. The films with smoother surface are more suitable for achieving better quality interface between the adjacent layers for fabricating high efficiency solar cell.

Figure 5 shows 2D and 3D AFM images of the Sb_2Se_3 thin films. Figure 5(a) shows the film as deposited with substrate heating. Figure 5(b) shows a film annealed at 100˚C. Figure 5(c) shows a film annealed at 200˚C and figure 5(d) shows a film annealed at 300˚C.

The as-deposited and annealed films show almost similar topography with roughness values falling between the ranges of 13.8 nm to 18 nm. All the films show smoother and tightly packed morphology. The roughness values are found to reduce slightly after the annealing. It can be observed from the SEM images that all the films exhibit smaller uneven grains with almost identical morphologies. The films with smoother surface are more suitable for achieving better quality interface between the adjacent layers while fabricating a solar cell.

Referring now to figure 6, there are shown two measured IV curves for a single junction Sb_2Se_3 solar cell fabricated with 300°C annealed films (a) and the I-V curve of a single junction wide band gap perovskite (FAPbI3-MAPbBr3) solar cell (b). The efficiency of Sb2Se3 based solar cell was around 5% and the efficiency of FAPbI3-MAPbBr3 based solar cell was around 12.4%. The parameters of two devices are given in following table from the respective two I-V curves.

Device	**J_{sc}**	**V_{oc}**	**FF**	**E_{ff}**
Sb_2Se_3 solar cell	20.1	0.45	56	5.07
$FAPbI_3$-$MAPbBr_3$ solar cell	18.5	1.05	64	12.43

Referring now to figure 7, there is shown a comparison of current-voltage characteristics of three different PV devices. Curve 72 is for a single layer Chalcogenide cell, curve 74 is for a single layer Perovskite cell, and curve 76 is for the Perovskite-Chalcogenide device 10 (as shown in figure 1) comprising both the Perovskite and Chalcogenide layers. The open circuit voltage for the Perovskite-Chalcogenide device 10 is V_{OC} = 1.5 V, which is approximately equal to sum of the open circuit voltages

for the single layer Chalcogenide cell (0.4 V) and the single layer Perovskite cell (1.1 V). The short circuit current for the device 10 is J_{SC} = 21 mA/cm^2, which is smaller than the short circuit current for the single layer Chalcogenide cell (24.1 mA/cm^2) and single layer Perovskite cell(21.8 mA/cm^2).

Device	J_{sc}	V_{oc}	FF	E_{ff}
Chalcogenide solar cell	24.1	0.42	55.6	5.6
Perovskite solar cell	21.8	1.1	77	18.4
Perovskite-Chalcogenide device	21	1.5	64	20.1

Table 1: Performance characteristics of Chalcogenide, Perovskite, and Perovskite-Chalcogenide device 10, where J_{sc}, V_{oc}, FF and E_{ff} correspond to short-circuit current density, open circuit voltage, fill factor and efficiency respectively.

Figure 8 shows simulated results for lifetime/stability characteristics of the conventional single layer Perovskite solar cell and Chalcogenide-Perovskite solar cell 10 as shown in figure 1. In figure 8, data sets 82 is for the conventional single layer Perovskite solar cell and it is evident from this data that the efficiency of these solar cells decreases with the lifetime/stability of Perovskite material. Data set 84 is for the Chalcogenide-Perovskite solar cell device 10 under high humidity conditions (85% humidity). Data set 84 shows that normalised efficiency is not affected for a lifetime of 60 days under extreme humid conditions. This stability in the efficiency of the Chalcogenide-Perovskite solar cell is a result of encapsulation of the Perovskite material using the Sb_2Se_3.

Antimony Selenide (Sb_2Se_3) is an inorganic semiconductor material exhibiting intrinsically benign grain boundaries (GBs) and possess strong covalent Sb-Se bonds. Furthermore the crystal growth along the (100) and (010) surfaces in Sb_2Se_3 require no breaking of the Sb-Se bonds and thus produce no dangling bonds. Absence of dangling bonds results in less-reactive sites for oxygen and water absorption. Hence the material is intrinsically highly stable as it does not allow water or oxygen molecules to pass through it and reach the adjacent perovskite layers.

Referring now to figure 9, there is shown a flow diagram 90 outlining a series of method steps to manufacture a PV device in accordance with embodiments. The first step 92 of the method consists in forming a first solar cell structure 21 on a substrate. The first solar cell structure comprises of a first photon absorbing layer 6 that comprises a material that has a Perovskite structure and having a first band gap. The substrate is typically coated with a conductive transparent oxide, such as ITO.

At step 94, a second solar cell structure 22 is formed. The second solar cell structure 22 comprises of a second photon absorbing layer comprising an inorganic material that has a Chalcogenide structure and having a second band gap. The second solar cell 22 is positioned at least partially onto the first solar cell 21.

At step 96, the second solar cell 22 is arranged to be in electrical contact with the first solar cell 21 and to provide encapsulation of the first solar cell. The photovoltaic device 10 is arranged such that received photons are absorbed by at least one of the first and the second solar cells.

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.

The term "comprising" (and its grammatical variations) as used herein are used in the inclusive sense of "having" or "including" and not in the sense of "consisting only of".

The Claims as defined in the invention are as follows:

1. A photovoltaic device comprising:

a photon receiving surface;

a first photon absorbing layer comprising a material that has a Perovskite structure and having a first bandgap; and

a second photon absorbing layer comprising an inorganic material that has a Chalcogenide structure and having a second bandgap; the first photon absorbing layer being positioned at least partially between the photon receiving surface and the second photon absorbing layer;

wherein the second photon absorbing layer is arranged to provide encapsulation for at least a portion of the first photon absorbing layer and the photovoltaic device is arranged such that received photons are absorbed by at least one of the first and the second photon absorbing layers.

2. The device of claim 1 wherein the first photon absorbing layer comprises a Methylammonium Lead Bromide ($CH_3NH_3PbBr_3$) Perovskite.

3. The device of claim 1 or claim 2 wherein the second photon absorbing layer comprises antimony selenide (Sb_2Se_3).

4. The device of claim 3 wherein the thickness of the Sb_2Se_3 is comprised between 200nm to 1µm.

5. The device of any one of the preceding claims wherein the device has an energy conversion efficiency that is

higher than the energy conversion efficiency of a Perovskite photovoltaic device with a single photon absorbing layer similar to the first photon absorbing layer by at least 8% relative.

6. The device of any one of the preceding claims wherein the degradation of the energy conversion efficiency is lower than 2% for a period of at least 60 days.

7. The device of any one of the preceding claims wherein the second photon absorbing layer is arranged to reduce the amount of moisture reaching the first photon absorbing layer by 50% relative when compared to a Perovskite photovoltaic device with a single photon absorbing layer similar to the first photon absorbing layer.

8. The device of any one of the preceding claims wherein the second photon absorbing layer is arranged to reduce the amount of moisture reaching the first photon absorbing layer by 95% when compared to a Perovskite photovoltaic device with a single photon absorbing layer similar to the first photon absorbing layer.

9. The device of any one of the preceding claims wherein the device further comprises a silver or gold interconnecting layer disposed between the first and the second photon absorbing layers; the silver layer having a thickness comprised between 2nm and 5nm.

10. The device of claim 9 wherein the interconnecting layer is arranged to reflect a portion of high energy photons that have entered the device towards the second photon absorbing layer.

11. The device of any one of the preceding claims wherein the device further comprises a wide bandgap n-type metal oxide layer comprising TiO_2 or ZnO nanoparticles disposed between the photon receiving surface and the first photon absorbing layer; the layer being arranged as an electron transport layer which facilitates the transport of electrons from the photovoltaic device to a contact structure.

12. The device of any one of the preceding claims wherein the device further comprises a WO_3 layer, disposed between the second photon absorbing layer and a rear contact of the photovoltaic device, arranged as a hole transport layer which facilitates the transport of holes from the photovoltaic device to a contact structure.

13. The device of any one of the preceding claims wherein the first bandgap is larger than the second bandgap.

14. The photovoltaic device according to any one of the preceding claims wherein the Perovskite material is a self-assembled material.

15. The photovoltaic device according to any one of the preceding claims wherein the Perovskite material comprises an inorganic-organic compound.

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

forming a first solar cell structure on a substrate, the first solar cell structure comprising a first photon absorbing layer that comprises a material that has a Perovskite structure and having a first bandgap; and

forming a second solar cell structure comprising a second photon absorbing layer comprising an inorganic material that has a Chalcogenide structure and having a second bandgap; the second solar cell being positioned at least partially onto the first solar cell;

wherein the second solar cell is in electrical contact with the first solar cell and is arranged to provide encapsulation of the first solar cell; and the photovoltaic device is arranged such that received photons are absorbed by at least one of the first and the second solar cells.

17. The method of claim 16 wherein the method further comprises the step of depositing a silver or gold interconnecting layer between the steps of forming the first and the second solar cells; the interconnecting layer having a thickness comprised between 2nm and 5nm and being arranged to reflect a portion of high energy photons that have entered the device towards the second photon absorbing layer.

18. The method of claim 17 wherein the method further comprises the step of selecting at least one property of the silver layer to tune the optical field distribution within the photovoltaic device.

19. The method of any one of claims 16 to 18 wherein the first photon absorbing layer comprises a Methylammonium Lead Bromide ($CH_3NH_3PbBr_3$) Perovskite.

20. The method of any one of claims 16 to 19 wherein the second photon absorbing layer comprises antimony selenide (Sb_2Se_3).

21. The method of any one of claims 16 to 20 wherein the step of forming a second solar cell structure comprises the step of evaporating Sb_2Se_3 at a vacuum pressure between 6 and 10 mTorr from a Sb_2Se_3 powder source or spin coating a solution containing Sb_2Se_3.

22. The method of any one of claims 16 to 21 wherein the step of forming a second solar cell structure is performed in a manner to reduce the amount of moisture reaching the first photon absorbing layer by 50% relative when compared to a Perovskite photovoltaic device with a single photon absorbing layer similar to the first photon absorbing layer.

23. The method of any one of claims 16 to 22 wherein the method further comprises the step of forming a layer comprising TiO_2 or ZnO nanoparticles disposed between the photon receiving surface and the first photon absorbing layer; the layer being arranged as an electron transport layer which facilitates the transport of electrons from the photovoltaic device to a contact structure.

24. The method of any one of claims 16 to 23 wherein the method further comprises the step of forming WO_3 layer between the second photon absorbing layer and a rear contact of the photovoltaic device; the WO_3 layer comprising WO_3 being arranged as an hole transport layer which facilitates the transport of holes from the photovoltaic device to a contact structure.

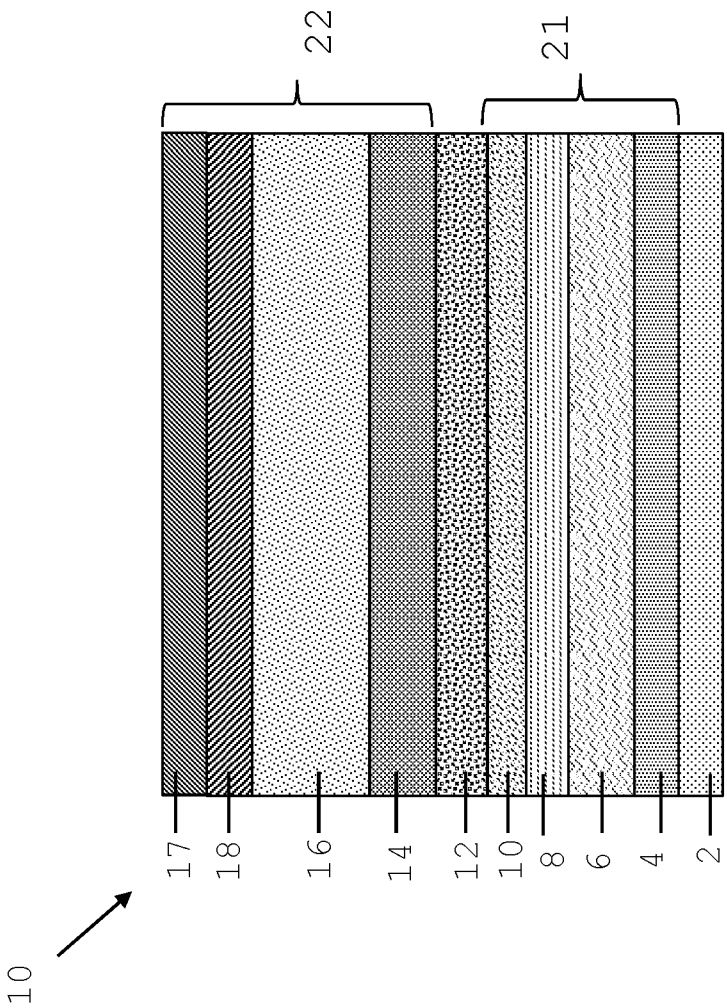

FIGURE 1

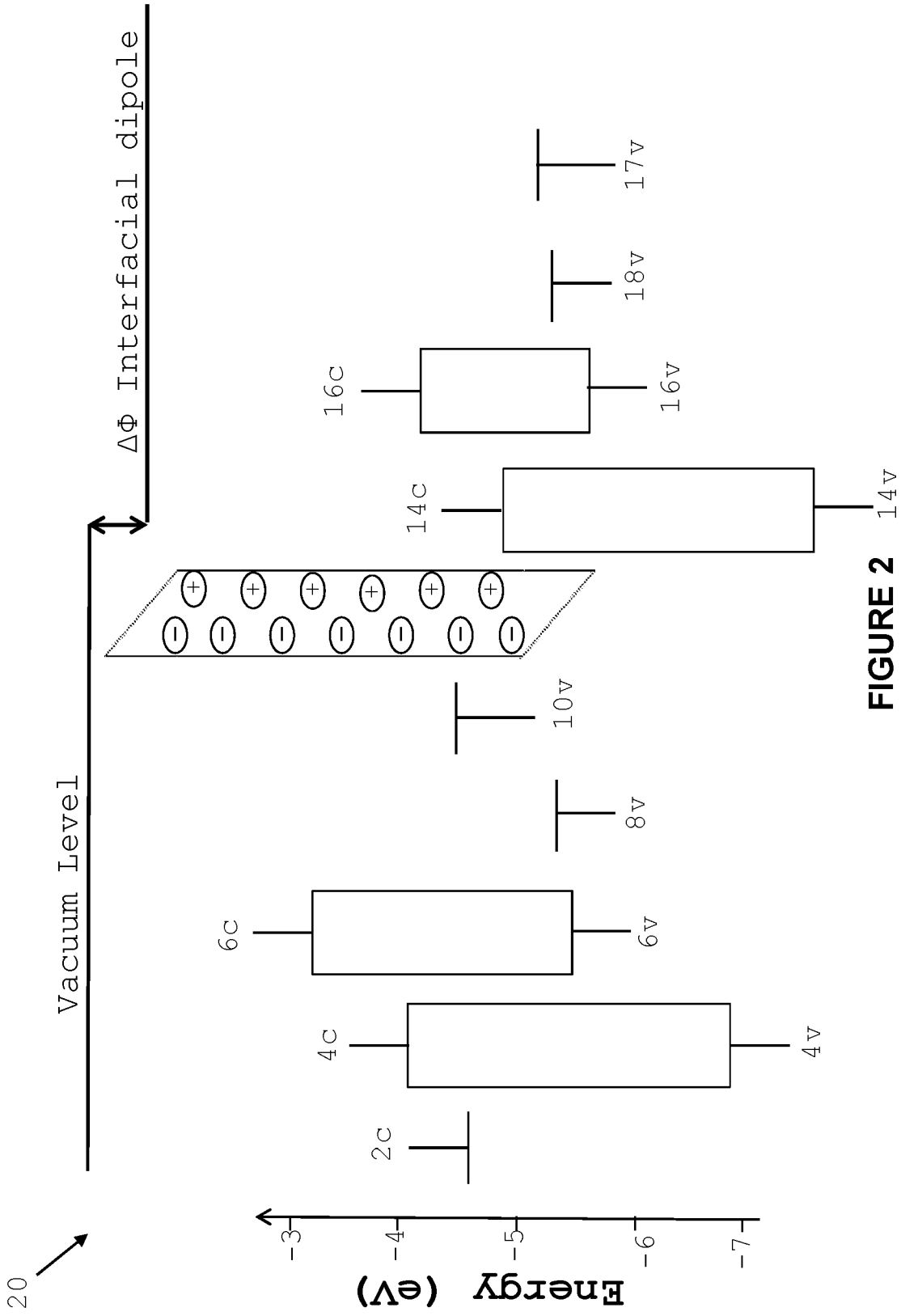
20
Energy (eV)
-3
-4
-5
-6
-7
Vacuum Level
ΔΦ Interfacial dipole
2c
4c
4v
6c
6v
8v
10v
14c
14v
16c
16v
18v
17v

FIGURE 2

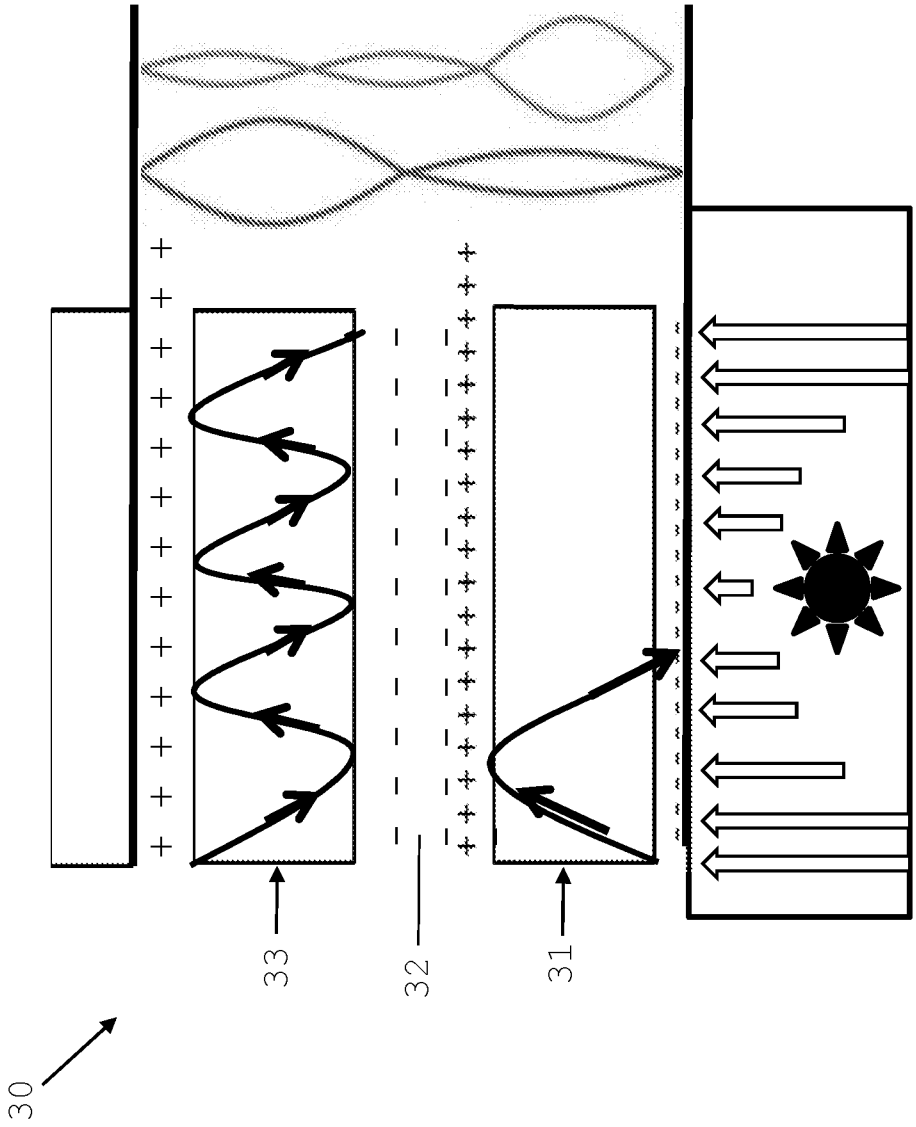

FIGURE 3

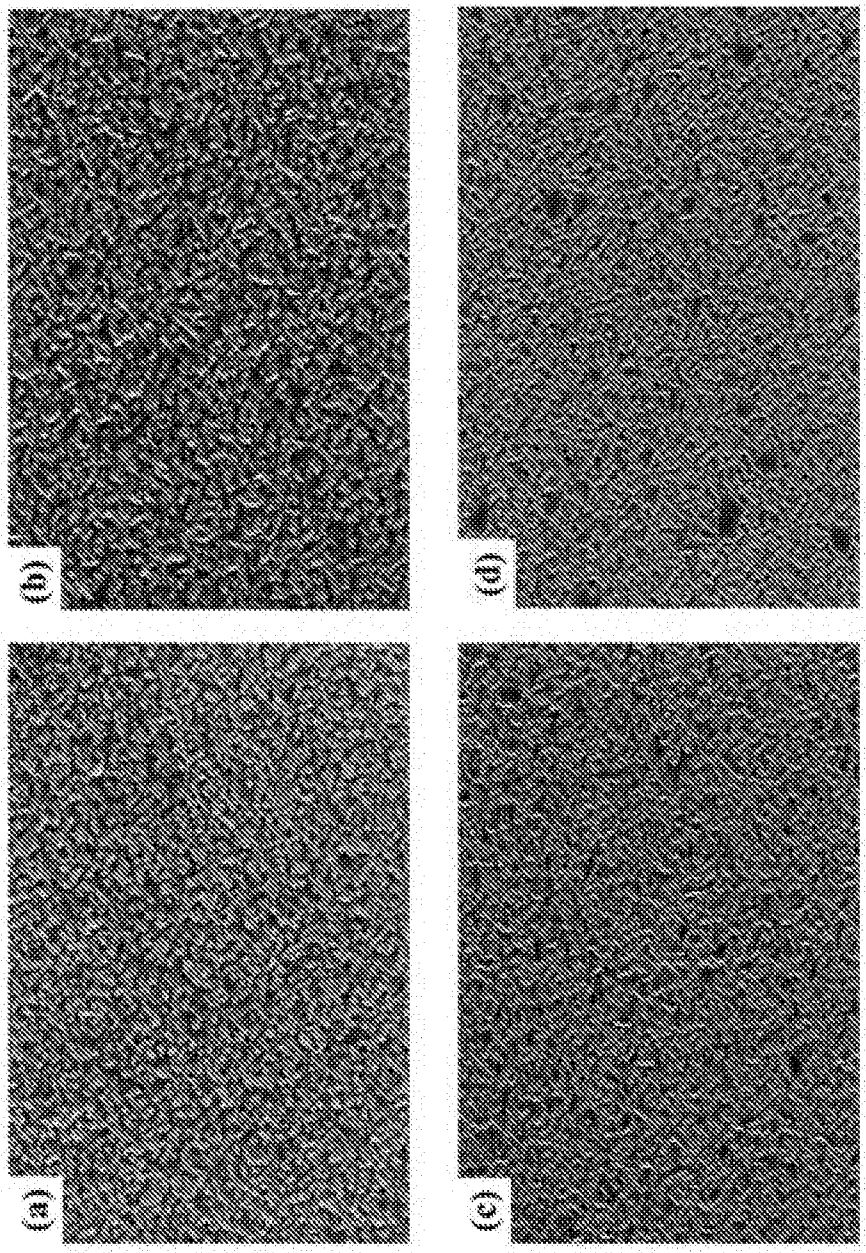

FIGURE 4

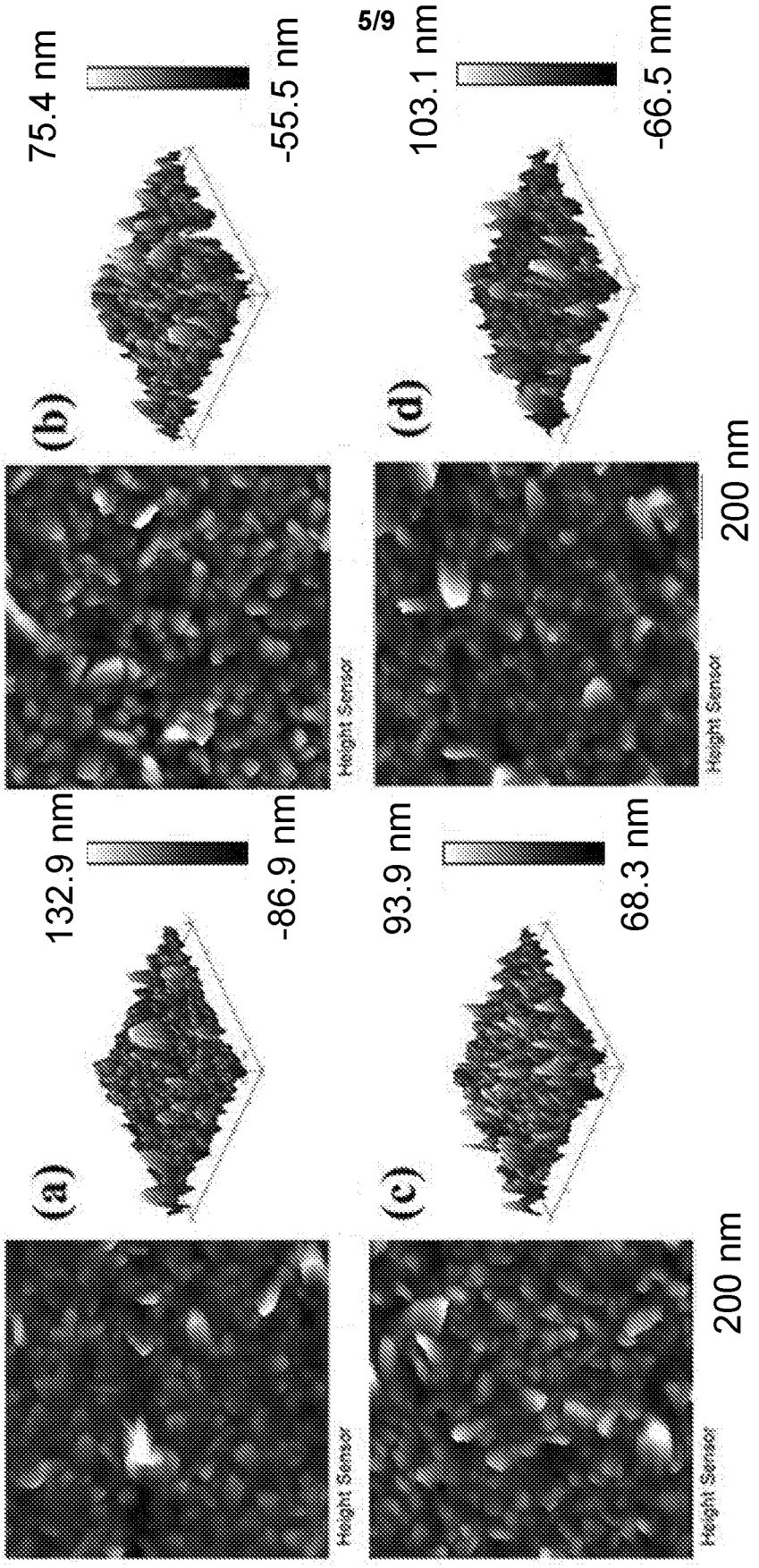
(a)
132.9 nm
-86.9 nm
Height Sensor
200 nm
(b)
75.4 nm
-55.5 nm
Height Sensor
200 nm
(c)
93.9 nm
68.3 nm
Height Sensor
200 nm
(d)
103.1 nm
-66.5 nm
Height Sensor
200 nm

FIGURE 5

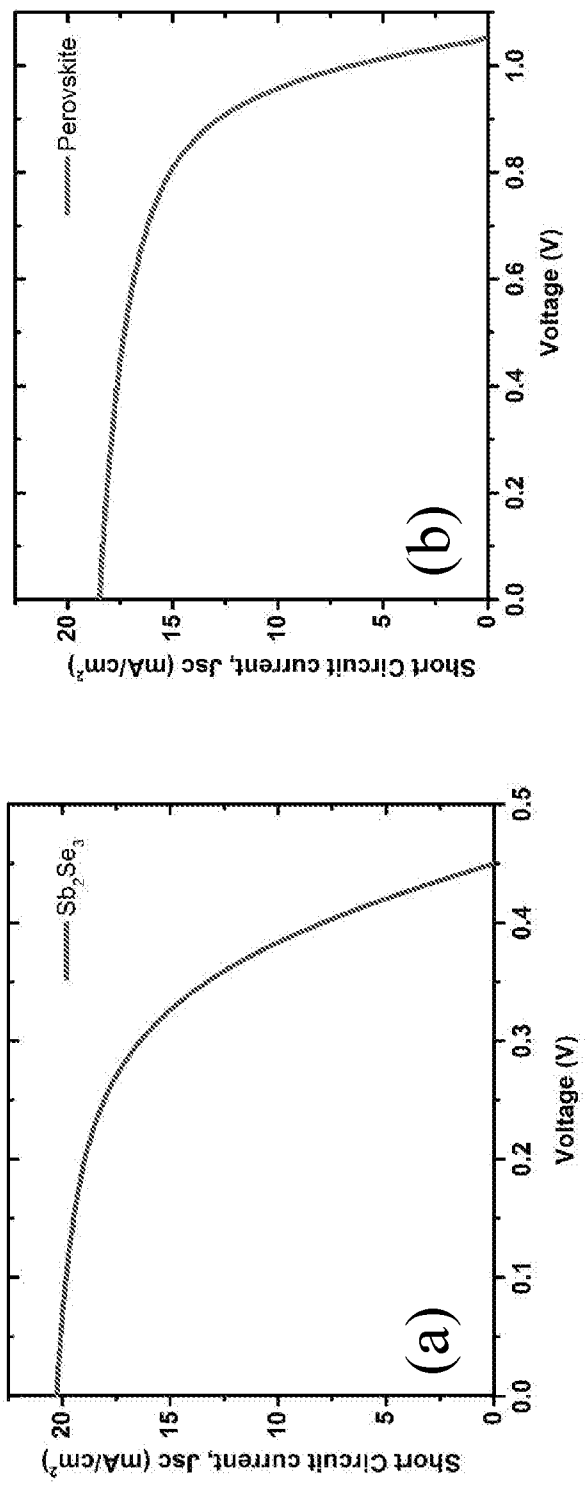
Short Circuit current, Jsc (mA/cm²)
Voltage (V)
Sb2Se3
(a)
Perovskite
(b)

FIGURE 6

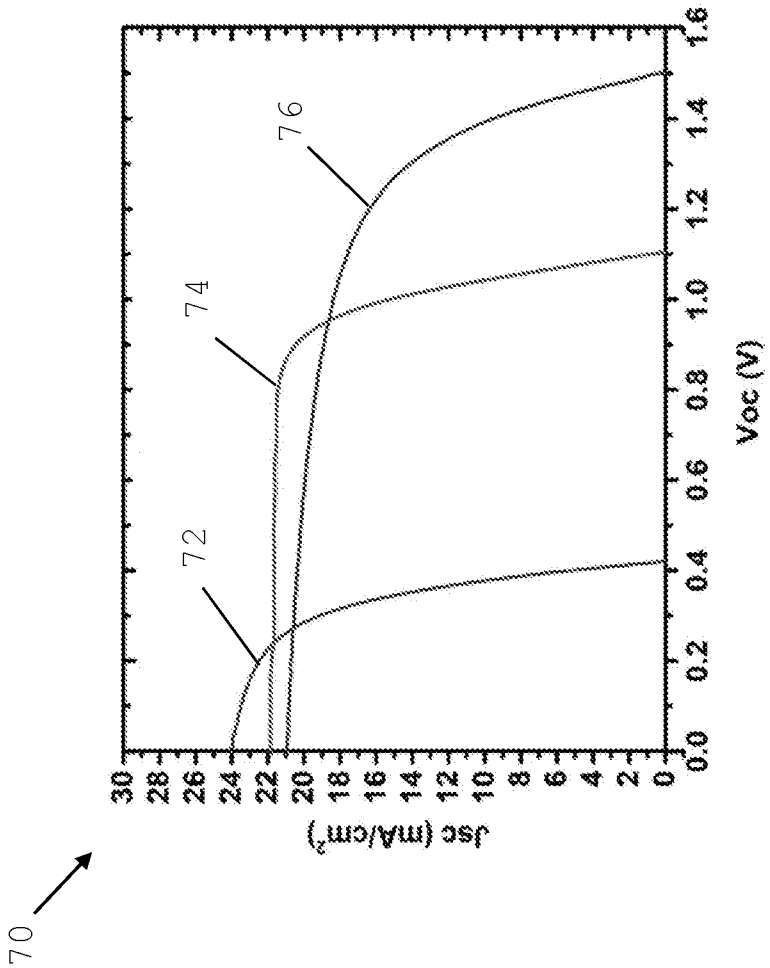
70
72
74
76
Jsc (mA/cm²)
Voc (V)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

FIGURE 7

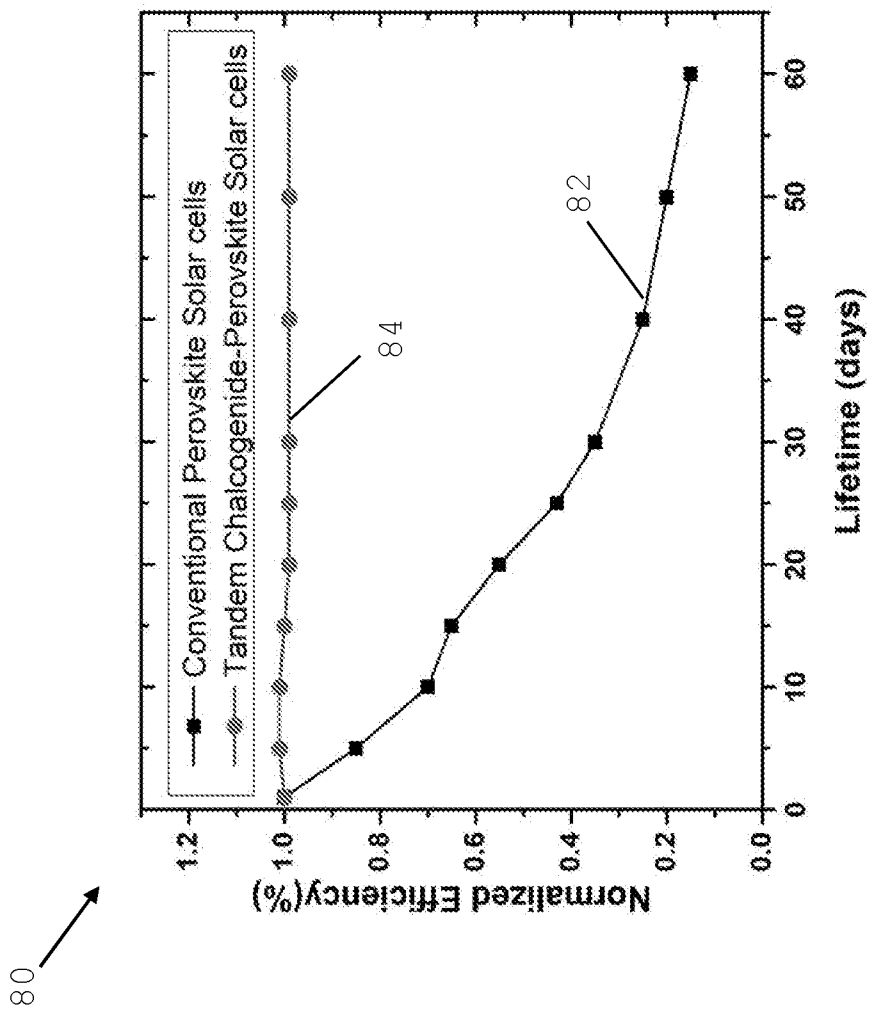
80
Conventional Perovskite Solar cells
Tandem Chalcogenide-Perovskite Solar cells
82
84
Normalized Efficiency(%)
Lifetime (days)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
10
20
30
40
50
60

FIGURE 8

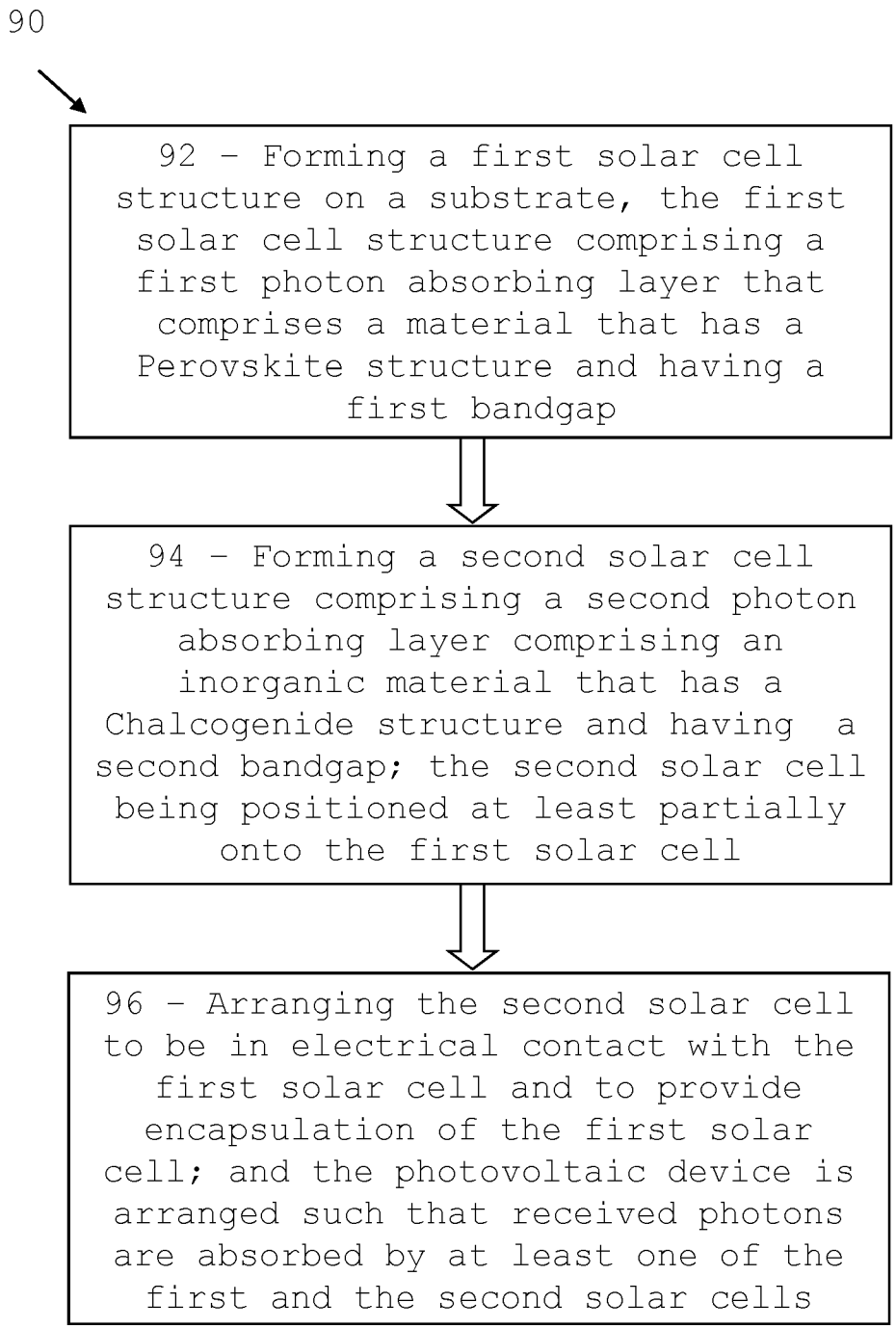
90
92 – Forming a first solar cell structure on a substrate, the first solar cell structure comprising a first photon absorbing layer that comprises a material that has a Perovskite structure and having a first bandgap
94 – Forming a second solar cell structure comprising a second photon absorbing layer comprising an inorganic material that has a Chalcogenide structure and having a second bandgap; the second solar cell being positioned at least partially onto the first solar cell
96 – Arranging the second solar cell to be in electrical contact with the first solar cell and to provide encapsulation of the first solar cell; and the photovoltaic device is arranged such that received photons are absorbed by at least one of the first and the second solar cells

FIGURE 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2017/051115

A. CLASSIFICATION OF SUBJECT MATTER

H01L 31/0256 (2006.01) ***H01L 31/032 (2006.01)*** ***H01L 31/06 (2012.01)*** ***H01L 31/072 (2012.01)***
H01L 31/0725 (2012.01) ***H01L 31/075 (2012.01)*** ***H01L 31/18 (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)

Database: PATENW (EPODOC, WPIAP and English full text databases). IPC and CPC: H01L 31/--; H01L 27/142 (and sub-marks); H01L 51/42 (and sub-marks); H01G 9/20 (and sub-marks); H01L 31/04 (and sub-marks). CPC: Y02E 10/50 (and sub-marks); H01G 9/2068 (and sub-marks); H01L 21/02197. Keywords: photovoltaic, solar; perovskite, methylammonium lead bromide; antimony selenide; organic-inorganic perovskite; photon, light; absorb, absorption, sensitive; layer, coating, film, material; photoactive; chalcogenide, oxide, sulphide, selenide, telluride; CIGS, CIGSe, CIS, CISe, CZTS, CZTSe; reduce, stop, prevent, block, barrier; moisture, water; AND LIKE TERMS. Database: INSPEC. Search terms: perovskite, methylammonium lead bromide; Uddin (Author), Elumalai (Author); antimony selenide; photovoltaic, solar; chalcogenide, oxide, sulphide, selenide, telluride; CIGS, CIGSe, CIS, CISe, CZTS, CZTSe; stack, tandem; photon, light; absorb, absorption, sensitive; layer, coating, film, material; photoactive; reduce, stop, prevent, block, barrier; moisture, water; AND LIKE TERMS. Databases: Espacenet and Auspat. Search terms: Newsouth Innovations Pty Limited (Applicant); Ashraf Uddin (Inventor), Naveen Kumar Elumalai (Inventor); perovskite; AND LIKE TERMS. Applicant and Inventor names 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

"E" earlier application or patent but published on or after the international filing date

"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
19 December 2017	19 December 2017
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	Richard Baker AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832583

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2017/051115**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/0249170 A1 (ISIS INNOVATION LIMITED) 03 September 2015 Paragraphs 0004 to 0005, 0189, 0256 to 0258, 0275 to 0277, 0330 to 0348, 0456, figure 17	1-24
X	WO 2016/111576 A1 (KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY) 14 July 2016 & EP 3244455 A1 (KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY) 15 November 2017 Paragraphs 0097 to 0100, 0109, 0110, 0118, 0126, 0127, 0129, 0216, 0229 to 0230, 0234, 0241, 0278 to 0279, 0317 to 0323, 0327 and 0348	1-24

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2017/051115**

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**
US 2015/0249170 A1	03 September 2015	US 2015249170 A1	03 Sep 2015
		AU 2013319979 A1	19 Mar 2015
		AU 2013319979 B2	25 Aug 2016
		AU 2016204753 A1	28 Jul 2016
		AU 2016204753 B2	20 Apr 2017
		AU 2017203629 A1	15 Jun 2017
		CN 104769736 A	08 Jul 2015
		CN 104769736 B	24 Aug 2016
		CN 106206952 A	07 Dec 2016
		CN 106684246 A	17 May 2017
		EP 2898553 A1	29 Jul 2015
		JP 2015535390 A	10 Dec 2015
		KR 20150056851 A	27 May 2015
		WO 2014045021 A1	27 Mar 2014
WO 2016/111576 A1	14 July 2016	WO 2016111576 A1	14 Jul 2016
		CN 107431128 A	01 Dec 2017
		EP 3244455 A1	15 Nov 2017
		KR 20160085720 A	18 Jul 2016
		KR 101755333 B1	10 Jul 2017
		KR 20170070855 A	22 Jun 2017

End of Annex

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