

PEROVSKITE SOLAR CELL

FIELD OF THE DISCLOSURE

5 The present disclosure relates to a method of manufacturing a perovskite solar cell and a perovskite solar cell.

BACKGROUND OF THE DISCLOSURE

10 Solar cells based on perovskite materials represent a promising development in photovoltaic technology. Known perovskite solar cells have a light-absorber layer which comprises a perovskite-structured compound, which typically includes a hybrid organic-inorganic lead, or tin, halide-based material, that is configured to absorb solar radiation.

15 A general aim for perovskite solar cell development is to attain high power conversion efficiency by suppressing chemical instabilities in the perovskite material caused by defects in the crystal structure and increasing charge-carrier mobility. These defects also lead to excessive charge recombination, which eliminates charge-carriers and thus reduces the density of photogenerated charge carriers flowing through the solar cell.

20 Efforts to address these problems have focussed on immobilising the defects within the crystal structure to achieve stable perovskite solar cells with increased photovoltaic performance. Despite these developments, there remains a need to improve the passivation of defects in perovskite solar cells.

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SUMMARY OF THE DISCLOSURE

A first aspect of the present disclosure provides a method of manufacturing a perovskite solar cell. The solar cell comprises a light-absorber layer comprising a perovskite material and a
30 hole-transport layer comprising a p-type doped semiconductor material. The method comprises: forming a perovskite material on a substrate to form the light-absorber layer; forming the p-type doped semiconductor material on the substrate to define the hole-transport layer; and passivating one or more layers of the solar cell with a passivating medium comprising boron trifluoride, the one or more layers selected from the group consisting of: the
35 light-absorber layer and the hole-transport layer; wherein the step of passivating the one or

more layers comprises directing a flow of gas comprising boron trifluoride towards said one or more layers or the substrate said one or more layers are to be formed on.

Without wishing to be bound by theory, the inventors consider that the introduction of the boron trifluoride in a gaseous form causes passivation of the perovskite material in the light-absorber layer and the passivation and/or elimination of defects in the p-type doped semiconductor material of the hole-transport layer that would otherwise trap charge carriers, both of which thereby improve the performance of the solar cell. The boron trifluoride gas molecules are able to behave as both a Lewis acid (electron acceptor) and as a Lewis base (electron donor) to simultaneously bond with cations and anions on a surface, and at grain boundaries (e.g. at a surface of, and at grain boundaries of, the perovskite material and/or the p-type doped semiconductor material). In particular, the boron trifluoride gas molecules produce fluoride ions which form strong bonds with uncoordinated metal cations (e.g. lead ions, Pb^{2+}) in the perovskite crystal structure. The passivation of such defects helps to suppress non-radiative recombination losses within the light-absorber layer and/or hole-transport layer, which thereby increases the operating efficiency of the solar cell.

The boron trifluoride gas molecules also suppress phase changes within the perovskite crystal structure, thereby increasing the stability of the perovskite material. For example, the boron-trifluoride gas molecules also produce ions which bond to halide ions (e.g. iodide ions, I^-) in the perovskite crystal structure, and thereby inhibit the movement of the halide ions. This slows the crystallisation process of the perovskite material (which improves the crystalline quality), which thereby improves the quality of the light-absorber layer. The boron trifluoride gas molecules can also increase the hydrophobicity of the perovskite material surface and/or the p-type doped semiconductor material surface to further improve the stability of the light-absorber layer and/or hole-transport layer.

A known method of making a perovskite solar cell is described in Nano-Micro Letters volume 13, Article number: 169 (2021). This method involves adding a solid chemical compound (or additive) to a perovskite precursor solution during the fabrication of the solar cell. The solid chemical additive ((benzylamine)trifluoroboron) includes a solid complex of boron and fluorine atoms which passivate the perovskite material. The method according to the present invention provides a means of delivering the boron trifluoride molecule to the perovskite material and/or p-type doped semiconductor material in a gaseous form, which enables passivation of the perovskite material and/or p-type doped semiconductor material to be controlled (e.g. by adjusting the flow of gaseous boron trifluoride) during the solar cell manufacturing method.

Optional features will now be set out. These are applicable singly or in any combination with any aspect.

5 Control of the application of boron trifluoride to layers the solar cell is important because the perovskite layer is fragile, and BF₃ may have other deleterious effects on the perovskite layer if applied, for example, at high pressures and/or high concentrations. Accordingly, it may also be advantageous to apply the flow of gas comprising boron trifluoride to just the hole-transport layer.

10 It will be appreciated that the flow of gas which is directed towards the substrate may comprise a plurality of gaseous species (e.g. a mixture of two or more gases). It will be appreciated that the flow of gas may be directed generally towards the solar cell (e.g. the constituent components of the solar cell), without diverging from the scope of the present disclosure. The
15 flow of gas may be configured such that gaseous boron fluoride molecules are present in the environment near to the solar cell (e.g. in the near vicinity of solar cell) in order to facilitate passivation of the perovskite material and/or p-type doped semiconductor material.

The step of passivating the one or more layers may comprise directing the flow of gas comprising boron trifluoride towards the substrate (e.g. towards the perovskite material and/or
20 p-type doped semiconductor material arranged on the substrate) during the formation (e.g. deposition) of the layers on the substrate. Alternatively, or in addition, the boron-trifluoride containing gas may be directed towards the substrate after the perovskite material and/or p-type doped semiconductor material is formed (e.g. deposited) on the substrate.

25 The step of passivating the one or more layers may comprise directing the flow of gas comprising boron trifluoride towards the substrate before the layers are formed thereon. In this way, the method may comprise configuring the local (e.g. immediate) atmosphere surrounding the solar cell with passivating gas molecules and/or adsorbing passivating gas molecules onto
30 an existing surface of the solar cell in anticipation of forming the perovskite material and/or the p-type doped semiconductor material, to facilitate passivation thereof.

The method of passivating the solar cell may be carried out using an apparatus for passivating the solar cell. The method may comprise inserting an at least partially fabricated solar cell into
35 a passivation chamber of the apparatus and directing a flow of gas (e.g. a gas mixture) into the passivation chamber.

The flow of gas into the passivation chamber may be controlled by operating a gas flow control device of the apparatus. The apparatus may comprise a gas reservoir configured to store the passivating medium (e.g. the boron trifluoride gas). The gas reservoir may comprise a plurality
5 of gas stores each of which may be configured to store a different type of gas, or gas mixture (e.g. ammonia gas, nitrogen gas, and boron trifluoride gas, or any mixture thereof). The passivating method may end by stopping the gas flow into the passivation chamber, and/or removing the solar cell from the passivation chamber.

10 The pressure in the passivating chamber during the step of passivating the one or more layers of the solar cell (e.g. the pressure of the gas comprising boron trifluoride in the passivating chamber) may be between 10^{-4} mbar and 10^{-6} mbar.

The percentage concentration by volume of boron trifluoride gas in the flow of gas may be
15 between 0.1% to 10%. The remainder of the gas may comprise, or consist of, chemically inert gas. For example, the remainder of the gas may comprise, or consist of, at least one of nitrogen, argon, or any other suitable inert gas. The percentage concentration by volume of boron trifluoride gas in the flow of gas may be greater than or equal to 0.1%, greater than or equal to 0.5%, greater than or equal to 1%, greater than or equal to 2%, greater than or equal
20 to 3%, greater than or equal to 4%, greater than or equal to 5%, greater than or equal to 6%, greater than or equal to 7%, greater than or equal to 8%, or greater than or equal to 9%. The percentage concentration by volume of boron trifluoride gas in the flow of gas may be less than or equal to 0.5%, less than or equal to 1%, less than or equal to 2%, less than or equal to 3%, less than or equal to 4%, less than or equal to 5%, less than or equal to 6%, less than or equal
25 to 7%, less than or equal to 8%, less than or equal to 9%, or less than or equal to 10%.

The flow of gas may further comprise ammonia (e.g. ammonia gas). The percentage concentration by volume of ammonia gas in the flow of gas may be between 0.1% to 10%. On combining with ammonia gas, the boron trifluoride gas molecules form a Lewis adduct
30 ($\text{NH}_3:\text{BF}_3$) which can act as zwitterion to passivate both anionic and cationic defects in the perovskite material. The remainder of the gas may consist of a chemically inert gas (e.g. comprising one or more of N_2 and Ar).

35 The step of forming the perovskite material and/or the step of forming the p-type doped semiconductor material may comprise a vapour-based deposition process which may be

selected from the group consisting of: sputtering, chemical vapour deposition, and plasma-enhanced chemical vapour deposition.

5 The step of forming the perovskite material and/or the step of forming the p-type doped semiconductor material may comprise a solution deposition process which may be selected from the group consisting of slot-die coating, dip-coating, spray-coating and spin coating. Where the step of forming the perovskite material and/or the step of forming the p-type doped semiconductor material comprises a solution deposition process, the flow of gas comprising boron trifluoride may be at ambient temperature, for example between 15°C and 30°C (e.g.
10 about 25°C). Where the step of forming the perovskite material and/or the step of forming the p-type doped semiconductor material comprises a solution deposition process and the passivating step is to be applied to said layer formed by a solution deposition process, the solution deposition process may be conducted in a passivation chamber. In this way, boron trifluoride gas, which is toxic, can be contained during the passivation step.

15 The solar cell may comprise a plurality of device layers which, together, define a mesoscopic, or planar heterojunction, device architecture. The solar cell may comprise the light-absorber layer interposed between a first electrode and a second electrode. One of the electrodes may define a negative electrode (e.g. an electron collecting electrode) and the other of the
20 electrodes may define a positive electrode (e.g. a hole collecting electrode).

The hole-transport layer may be interposed between the light-absorber layer and the first electrode (i.e. the positive/hole collecting electrode). The solar cell may further comprise an electron-transport layer interposed between the light-absorber layer and the second electrode
25 (i.e. the negative/electron collecting electrode). The electron-transport layer may comprise an n-type doped semiconductor material. The hole-transport layer may be configured in use to transport holes between the light-absorber layer and the positive electrode of the solar cell. The electron-transport layer may be configured in use to transport electrons between the light-absorber layer and the negative electrode of the solar cell. Each carrier-transport layers (i.e.
30 the hole-transport layer or the electron-transport layer) may be configured as a buffer between the light-absorber layer and the corresponding electrode, such that they may be configured to cause selective carrier extraction from the light-absorber layer.

Each of the electrodes may be configured, in use, to extract charge carriers from the respective
35 transport layers. Together, the negative electrode and the electron-transport layer may define a p-type contact (or negative electrode assembly) of the solar cell. The positive electrode and

the hole-transport layer may together define an n-type contact (or positive electrode assembly) of the solar cell.

5 The method of forming the charge-transport layer may comprise arranging (e.g. depositing) a semiconductor material between the light-absorber layer and the respective electrode (e.g. the positive electrode) to define a charge-transport layer (e.g. a hole-transport layer). The method may comprise arranging the charge-transport layer (e.g. hole-transport layer) onto the substrate and then depositing the light-absorber layer on top of the charge-transport layer. Alternatively, the method may comprise depositing the charge-transport layer (e.g. hole-transport layer) onto a light-absorber layer which is already arranged on the substrate, and then arranging an electrode on top of the charge-transport layer.

15 The method may comprise passivating the hole-transport layer by directing the flow of gas comprising boron trifluoride towards the p-type doped semiconductor material simultaneously with and/or subsequently to the step of forming the p-type doped semiconductor material to define the hole-transport layer. The passivation method may be enacted during the deposition of the hole-transport layer and/or as a separate passivation step of the solar cell manufacturing method.

20 The method may comprise passivating the hole-transport layer by directing the flow of gas comprising boron trifluoride towards the substrate prior to the step of forming the p-type semiconductor material to define the hole-transport layer. In this way, the method may comprise configuring the local (e.g. immediate) atmosphere surrounding the solar cell with passivating gas molecules and/or adsorbing passivating gas molecules onto an existing surface of the solar cell in anticipation of forming the p-type doped semiconductor material, to facilitate passivation thereof.

30 The boron trifluoride gas can act as passivating / additive species in the hole-transport layer and facilitate improved extraction of charge carriers (e.g. electrons) from the solar cell, e.g. because fewer charge carriers are being trapped by defects in the hole-transport layer.

35 According to the exemplary method, the perovskite material of the light-absorber layer may be subjected to a first passivation treatment, which may comprise directing a first gas mixture comprising boron trifluoride gas towards the substrate. Alternatively, or in addition, the perovskite material may be passivated according to a second passivation treatment which may

comprise directing a second gas mixture comprising boron trifluoride gas and ammonia gas towards the substrate.

5 The hole-transport layer may be passivated with at least one of the first and second passivation treatments. Indeed, the method may comprise passivating each of the light-absorber layer and the hole-transport layer using at least one, or each, of the first and second passivation treatments. Alternatively, the method may comprise performing only a single passivation treatment on at least one, or each, of the light-absorber and hole-transport layers. By way of example, where the method of manufacturing the perovskite solar cell comprises forming the perovskite material prior to forming the p-type doped semiconductor material, the step of passivating one or more layers of the solar cell may comprise performing a first passivation treatment to passivate the perovskite material (e.g. prior to, simultaneously with, and/or subsequently to forming the perovskite material), and performing a second passivation treatment to passivate the p-type doped semiconductor material (e.g. prior to, simultaneously with, and/or subsequently to forming the p-type doped semiconductor material), wherein the step of forming the p-type doped semiconductor material is performed between the first passivation treatment and second passivation treatment. In an alternative example, where the method of manufacturing the perovskite solar cell comprises forming the p-type doped semiconductor material prior to forming the perovskite material, the step of passivating one or more layers of the solar cell may comprise performing a first passivation treatment to passivate the p-type doped semiconductor material (e.g. prior to, simultaneously with, and/or subsequently to forming the p-type doped semiconductor material), and performing a second passivation treatment to passivate the perovskite material (e.g. prior to, simultaneously with, and/or subsequently to forming the perovskite material), wherein the step of forming the perovskite material is performed between the first passivation treatment and second passivation treatment.

30 The perovskite material of the light-absorber layer may have a composition expressed by a general formula of ABX_3 . Accordingly, component A may be an organic monovalent cation and may be one or more of MA ($CH_3NH_3^+$), FA ($HC(NH_2)_2^+$), EA ($CH_2CH_3NH_3^+$), or an inorganic cation including one or more of Cs^+ and Rb^+ . Component B may be a transition metal divalent cation and may be one or more of lead(II) cation (Pb^{2+}) and tin(II) cation (Sn^{2+}). Component X may be a monovalent anion and may be one or more of chloride (Cl^-), bromide (Br^-) and iodide (I^-).

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The substrate may be a semiconductor material (e.g. silicon), or an insulator such as silicon dioxide (e.g. glass). It will be appreciated that the substrate is primarily configured to support (e.g. mechanically or structurally support) the other elements of the solar cell, and it does not contribute to the photovoltaic output of the device.

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At least one, or each, of the electrodes may comprise an electrically conductive material such that they enable the flow of charge carriers between the light-absorber layer and an external circuit of the solar cell. One of the first and second electrodes may define a positive electrode, and the other of the first and second electrodes may define a negative electrode.

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At least one, or each, of the first and second electrodes may comprise a metal, such as silver (Ag), gold (Au), aluminium (Al), or copper (Cu), or a metal alloy comprising one or more such metals. At least one, or each, of the first and second electrodes may comprise an electrically conductive material (e.g. a transparent conductive oxide, a metal, or metal alloy). The conductive material may be deposited using a vapour deposition process (e.g. sputtering, or thermal vapour deposition). A deposition mask may be used to control the deposition process so that electrodes are deposited onto the correct underlying surface of the substrate. The electrodes may be arranged so as to be in direct contact with the substrate (e.g. with no intermediate layers disposed between the electrodes and the substrate).

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The n-type semiconductor may be selected from a group of inorganic compounds including tin oxide (SnO_x , e.g. SnO_2), titanium oxide (TiO_x , e.g. TiO_2), zinc oxide (ZnO_x , e.g. ZnO), tungsten oxide (WO_x , e.g. WO_3), barium titanate (BaTiO_3), niobium oxide (Nb_2O_5), strontium titanate (SrTiO_3), tantalum oxide (Ta_2O_5), zinc titanate (ZnTiO_3), copper titanate (CuTiO_3). Each of these inorganic compounds may be doped with at least one of niobium (Nb), strontium (Sr), aluminium (Al) and zinc (Zn). Alternatively, the n-type semiconductor may be selected from a group of organic compounds including carbon 60 (C60) and Phenyl-C61-butyric acid methyl ester (PCBM).

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The p-type semiconductor may be selected from a group of inorganic compounds including molybdenum oxide (MoO_x e.g. MoO_3), vanadium oxide (Vox , e.g. V_2O_5), nickel oxide (NiO), copper oxide (CuO_x , e.g. CuO or Cu_2O), tungsten oxide (WO_3). Each of these inorganic compounds may be doped with at least one of lithium (Li), magnesium (Mg), chromium (Cr), gallium (Ga). Alternatively, the p-type semiconductor may be selected from a group of hybrid inorganic/organic compounds including copper (II) phthalocyanine (CuPc), CuSCN, Spiro-OMeTAD, Spiro-TTB, PTAA, PEDOT-PSS, P3HT, 2PACz, MeO-2PACz.

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It will be appreciated that any of the metal oxide compounds (e.g. of the n-type and p-type semiconductor materials) may be provided in a stoichiometric, non-stoichiometric, or doped form.

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The charge-transport layers may comprise inorganic and/or organic semiconductor materials, as described above. The inorganic semiconductor materials may be deposited using a vapour deposition process (e.g. plasma enhanced vapour deposition). The organic semiconductor materials, or compounds, may be solution processed (e.g. deposited in a liquid form, or from a liquid precursor), as will be appreciated by the skilled person. A deposition mask may be used to control the vapour and/or liquid deposition process(es) so that the charge-transport layer(s) is/are deposited onto the correct underlying surface(s) of the solar cell.

According to a second aspect of the present disclosure, there is provided a perovskite solar cell manufactured according to any one of the preceding statements. The solar cell may have a front surface (e.g. upon which light is incident in normal use) and a rear surface opposite the front surface. Accordingly, the front surface may be configured in use to substantially face the sun.

The solar cell may have a first and a second dimension (e.g. a width and a height, respectively), which are both parallel to a planar surface of the substrate upon which the solar cell may be arranged. The solar cell may be arranged (e.g. deposited) on an upper (e.g. front) surface of the substrate (upon which light is incident in normal use). The solar cell may extend substantially across the entire length and/or the entire width of the substrate. The solar cell may comprise a third dimension (e.g. a height) which is perpendicular to the first and second dimensions, and is also perpendicular to the upper surface of the substrate upon which the solar cell is arranged.

According to a third aspect of the present disclosure, there is provided a method of manufacturing a perovskite solar module, the method of manufacturing the solar module comprising a step of executing the method of the first aspect to manufacture a perovskite solar cell.

A solar module (e.g. a solar panel) may define an apparatus for generating electrical power from sunlight. The solar module may comprise at least one solar cell which is arranged (e.g.

housed, or supported) by a structural frame, or housing. The at least one solar cell may be configured to absorb sunlight and generate electrical current.

5 The at least one solar cell may be configured with an electrical connector which enables electrical current to be extracted from the solar cell (e.g. to an electrical circuit of the solar module). The at least one solar cell and the electrical connector, when connected together, may define a solar cell assembly.

10 Two or more solar cells may be electrically connected in series (e.g. by one or more electrical connectors) to form a solar cell string. The solar module may comprise two or more solar cell strings, which may be electrically connected together in series and/or in parallel.

The solar module may comprise electrical circuitry which may be configured to extract electrical current from the solar panel to an external circuit (e.g. a second solar module).

15 It will be understood that the terms 'conductive' and 'insulating' as used herein, are expressly intended to mean electrically conductive and electrically insulating, respectively. The meaning of these terms will be particularly apparent in view of the technical context of the disclosure, being that of photovoltaic solar cell devices. It will also be understood that the term 'electrical connection' is intended to mean a non-rectifying electrical junction (i.e. a junction between two elements of the solar cell which exhibits a substantially linear current-voltage (I-V) characteristic).

25 It will be understood that when an element such as a layer, film, portion, region, or substrate is referred to as being "on" another element (e.g. being "formed on" another element), it can be directly on the other element or intervening elements may also be present. In contrast, when an element is referred to as being "directly on" another element, there are no intervening elements present. Furthermore, when an element is described as being 'interposed' between two other elements, then it can be directly interposed between those elements, or there may be additional intervening elements. In contrast, when an element is described as being 'directly' interposed between two other elements, then there are no intervening elements (e.g. there are only those three elements arranged together with one element interposed between the others).

35 The skilled person will appreciate that except where mutually exclusive, a feature or parameter described in relation to any one of the above aspects may be applied to any other aspect.

Furthermore, except where mutually exclusive, any feature or parameter described herein may be applied to any aspect and/or combined with any other feature or parameter described herein.

5 BRIEF DESCRIPTION OF THE DRAWINGS

Aspects and embodiments of the disclosure will now be described by way of example with reference to the accompanying drawings in which:

10 **Figure 1** is a transverse sectional view of a perovskite solar cell;

Figure 2 is a schematic drawing of an apparatus for passivating a perovskite solar cell; and

Figure 3 is a flowchart illustrating a method of manufacturing a perovskite solar cell.

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DETAILED DESCRIPTION

Aspects and embodiments of the present disclosure will now be discussed with reference to the accompanying figures. Further aspects and embodiments will be apparent to those skilled in the art.

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An exemplary perovskite solar cell 10, as manufactured according to a method of the present disclosure, will be described with reference to Fig. 1, which depicts a transverse section of the solar cell 10. In the drawings, the thickness of substrates, components, layers etc., may be exaggerated for clarity. Furthermore, it will be understood that when an element such as a layer, film, region, or substrate is referred to as being "on" another layer, it can be directly on the other layer or intervening layers may also be present. In contrast, when a layer is referred to as being "directly on" another layer, there are no intervening layers present.

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30 The solar cell 10 has a width which is the horizontal dimension of Fig. 1, and a height (e.g. a thickness) which is the vertical dimension. The solar cell 10 has a front surface 12 (upon which light is incident in normal use) and a back surface 14 opposite the front surface 12.

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The solar cell 10 comprises a plurality of device layers which define a mesoscopic, or planar heterojunction, device architecture. A light-absorber layer 20 is sandwiched between an electron-transport layer 16 and a hole-transport layer 18. Electrodes are arranged on the front

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and back surfaces 12, 14 of the solar cell 10 (e.g. such that the light-absorber layer 20 is interposed therebetween). A negative electrode 22 (e.g. an electron-collecting electrode) is arranged on the electron transport layer 16 and a positive electrode 24 (e.g. a hole-collecting electrode) is arranged on the hole-transport layer 18. Each of the electrodes 22, 24 is configured to extract charge carriers from the respective transport layers 16, 18, when the solar cell 10 is in use. Together, the negative electrode 22 and the electron-transport layer 16 define a p-type contact (or negative electrode assembly) of the solar cell 10. Similarly, the positive electrode 24 and the hole-transport layer 18 together define an n-type contact (or positive electrode assembly) of the solar cell 10.

The solar cell 10 is manufactured by sequentially building up the device layers onto a substrate 26, as would be understood by the skilled person. Considering Fig. 1, the solar cell 10 is orientated such that its front surface 12 is facing in a downward direction, which represents the orientation of the substrate 26 during the manufacture of the solar cell 10. The dashed arrows at the bottom of Fig. 1 show the direction of the solar radiation which is incident upon the solar cell 10. For example, during normal use, the solar cell 10 would be inverted from the orientation shown in Fig. 1 such that the front surface 12 is arranged to substantially face the sun.

The substrate 26 is made of an optically transparent material (e.g. glass) to allow solar radiation to reach the light-absorber layer 20. The negative electrode 22 comprises a transparent conducting oxide (TCO), to enable illumination of the light-absorber layer 20 from the front side of the device. The positive electrode 24, which is arranged on the back surface 14 of the solar cell is made of a metal, or metal alloy (e.g. Au). The hole-transport layer 18 is formed of a p-type semiconductor (e.g. Spiro-OMeTAD), whereas the electron-transport layer 16 is formed of an n-type semiconductor (e.g. TiO_2).

The light-absorber layer 20 comprises a perovskite-structured compound, which has a general formula of ABX_3 . Component A is an organic monovalent cation (e.g. methyl ammonium ion, CH_3NH_3^+), and component B is a transition metal divalent cation (e.g. lead, Pb^{2+}). Component X is a monovalent anion (e.g. Iodide, I). Accordingly, the perovskite-structured compound may have the formula $\text{CH}_3\text{NH}_3\text{PbI}_3$.

In use, the solar cell 10 is electrically coupled to an external circuit (not shown). Specifically, the external circuit is electrically connected to the electrodes of the solar cell 10. For example, the positive electrode 24 of the solar cell 10 is connected to a positive terminal of the electrical circuit, and the negative electrode 22 is connected to a negative terminal of the electrical circuit.

In such a solar cell 10, the absorption of photons by the hybrid perovskite material of the light-absorber layer 20 is followed by the formation and dissociation of excitons to produce separate positive and negative charge carriers (holes and electrons, respectively). The separated
5 charges move towards the respective p-type and n-type contacts. The electron- and hole-transport layers 16, 18 enhance the charge separation within the solar cell 10. For example, electrons are selectively transported into the electron-transport layer 16 and then extracted from the solar cell by the negative electrode 22. Similarly, the holes are selectively transported into the hole-transport layer 18 and then extracted by the positive electrode 24. The flow of
10 charges within the solar cell 10 is depicted by the curved dashed arrows shown in Fig. 1.

Fig. 2 shows an apparatus 30 for passivating a perovskite solar cell 10. The apparatus 30 is configured to passivate one or more of the constituent layers of the solar cell 10 (e.g. the light-absorber layer 20 and/or the hole-transport layer 18, as shown in Fig. 1). The apparatus 30
15 can also be configured to deposit at least one of the constituent layers of the solar cell 10, as will be described in more detail below.

The apparatus 30 comprises a passivation chamber 32 for receiving a solar cell 10 and a gas flow delivery system 60 for directing a flow of gas into the passivation chamber 32. The flow of
20 gas comprises boron trifluoride (BF_3) gas which passivates the perovskite material of the light-absorber layer 20 and/or the p-doped semiconductor material of the hole-transport layer 18, and thereby improves the performance of the solar cell 10.

The gas flow delivery system 60 includes a gas inlet 34, a gas reservoir 36, a gas flow control device 38, a controller 40, a gas outlet 42, and a pumping device 44. The gas flow delivery
25 system 60 is configurable to control the flow of passivating gas into the passivation chamber 32, as will be described in more detail below.

The passivation chamber 32 may be sized and configured to hold a plurality of solar cells 10 at the same time. For example, the plurality of solar cells 10 are positioned on a substrate carrier 46, as shown in Fig. 2. The apparatus 30 also includes a transport mechanism 48 for transporting the solar cell 10 and/or the substrate carrier 46, into the passivation chamber 32, and/or from the passivation chamber 32. The transport mechanism 48 may include a plurality
30 of rollers 50 on which to solar cell 10 and/or the substrate carrier 46 (see Fig. 2) is transported. The rollers 50 may be individually or collectively actuated by one or more motors such as electric motor (not shown).
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The passivation chamber 32 may include one or more walls 52 and is gas-tight such that a vacuum or low pressure can be generated within the passivation chamber 32. The passivation chamber 32 further includes an inlet door 54 and/or an outlet door 56 which each may be configured or act as a valve or sluice of the passivation chamber 32.

The solar cell 10 and/or a substrate carrier 46 can enter the passivation chamber 32 via the inlet door 54 (for example, the inlet door 54 opens when the transport mechanism 48 moves the solar cell 10 and/or the substrate carrier 46 into the passivation chamber 32). The solar cell 10 and/or a substrate carrier 46 can exit the passivation chamber 32 via the outlet door 56 (for example, the outlet door 56 opens when the transport mechanism 48 moves the solar cell 10 and/or the substrate carrier 46 out of the passivation chamber 32). When opening the inlet door 54 and/or the outlet door 56, the pressure in the passivation chamber 32 can be maintained or substantially maintained. This can allow a continuous operation of the apparatus 30 since the solar cell 10 and/or the substrate carrier 46 can enter the passivation chamber 32 at one end and exit the passivation chamber 32 at another end. Further, the passivation chamber 32 may be in fluid connection with further vacuum chambers (not shown in figures). For example, the further vacuum chambers may be configured for deposition of one or more of the device layers of the solar cell 10.

The gas reservoir 36 includes a plurality of gas stores each of which is configured to store a different type of gaseous species, or gas mixture, and can include a (separate) gas tank. In the embodiment depicted in Fig 1, the gas reservoir 36 includes a first gas store 62, a second gas store 64, and a third gas store 66. The first gas store 62, the second gas store 64 and the third gas store 66 are filled with boron trifluoride (BF_3) gas, nitrogen (N_2) gas, and ammonia (NH_3) gas, respectively. In use, the boron trifluoride and ammonia gases each define passivating gases which are able to passivate defects in the device layers of the solar cell 10. The nitrogen gas is used as an inert carrier gas which is mixed with passivating gases to control the concentration and flow rate of the gas being directed into the passivation chamber 32.

The gas flow control device 38 controls the flow of gas from the gas reservoir 36 into the passivation chamber 32. Thus, the gas flow control device 38 controls which gaseous species and the relative and absolute amounts thereof are supplied to the passivation chamber 32.

The gas flow control device 38 is positioned on a gas flow path between the gas reservoir 36 and the gas inlet 34 to the passivation chamber 32. The gas flow control device 38 is provided

for controlling the amount of gas that flows from each gas store 62, 64, 66 into the passivation chamber 32. In the embodiment shown in Fig. 1, the gas flow control device 38 includes a mixing device such as one or more taps or distribution device. The mixing device includes a plurality of input ports, each of which is connected to a respective gas store 62, 64, 66, for example via a pipe. The mixing device includes an output port which is connected to the gas inlet 34 and three valves, each valve controlling the amount of gas that flows from a respective input port to the output port. The gas flow control device 38 may include one or more (electrical) motors (i.e. actuators) for controlling the valves and thus the gas flow.

10 The gas inlet 34 is an opening within the passivation chamber 32 through which gas can be supplied to the passivation chamber 32. In the embodiment shown in Fig. 1, a multi-orifice plate 35 is provided as part of the gas inlet 34 and is configured to distribute the inflowing gas throughout the passivation chamber 32.

15 The pumping device 44 is fluidly connected to the gas outlet 42, e.g. via a pipe. The gas outlet 42 is an opening within the wall 36 of the passivation chamber 32 allowing the outflow of gas from the passivation chamber 32. In the embodiment shown in Fig. 1, the gas outlet 42 is positioned below the solar cell 10 and/or the transport mechanism 48.

20 The pumping device 44 includes one or more vacuum pumps such that the pumping device 44 is configured to generate low pressure or vacuum within the passivation chamber 32. The pressure within the passivation chamber 32 can be controlled by the operation of the pumping device 44 (i.e. how much gas is pumped out of the passivation chamber 32) and/or by the inflow of gas controlled by the gas flow control device 38 (i.e. how much gas is supplied to the passivation chamber 32).

The controller 40 can include a processor or other electronic means for controlling electrical components. For example, the controller 40 is a computer positioned remotely from the passivation chamber 32. The controller 40 is electronically connected to the gas flow control device 38, the pumping device 44. The controller 40 is configured to control the operation of the gas flow control device 38 and/or the pumping device 44. Thus, the controller 40 can control the amount, pressure and composition of the gas within the passivation chamber 32. Further, the controller 40 may also be electronically connected to the transport mechanism 48 for controlling the transport of the solar cell 10 into and/or out of the passivation chamber 32. Accordingly, the controller 40 may know the position of the solar cell 10 and thus can decide when to start the passivation treatment.

The apparatus 30 may be configured to passivate one or more of the device layers of the solar cell 10 during (e.g. simultaneously with) the deposition of said layers on the substrate 26. For example, the apparatus 30 may be controlled to direct a flow of passivating gas into the passivation chamber 32 either before or during the deposition of the device layers. The apparatus 30 may also be controlled to passivate the layers after they have been deposited (e.g. sequentially), for example, by directing passivating gas into the passivation chamber after the device layers have been deposited.

As described above, the apparatus 30 can also be configured to deposit at least one of the constituent layers of the solar cell 10. For example, the apparatus 30 may be configured to deposit the light-absorber layer 20 and/or the hole-transport layer 18 onto the substrate 26 of the solar cell 10.

Commonly known techniques for depositing the constituent layers of the solar cell 10 onto the substrate 26 can be used. For example, the apparatus 30 may comprise a plasma generation device (not shown) which is configured to initiate and maintain a plasma within the passivation chamber 32. Accordingly, the apparatus 30 uses plasma-enhanced chemical vapour deposition (PECVD) for depositing the constituent layers of the solar cell 10 on the substrate 26. The plasma required for the PECVD is generated by the plasma generation device. The plasma generation device can include a frequency generator, a first electrode, and/or a second electrode, as would be understood by the skilled person.

In this arrangement of the apparatus 30, the controller 40 may be configured to control the passivation treatment, and the deposition of a constituent layer of the solar cell 10 on to the substrate 26. Thus, the controller 40 can execute a method for (in-situ) passivation of the solar cell 10 and/or a method of fabricating the solar cell 10.

Alternatively, the apparatus 30 may be configured to receive a solar cell 10 (e.g. a partially manufactured solar cell) comprising one or more constituent layers which have been fabricated elsewhere (e.g. in a separate deposition system). In an exemplary arrangement, at least one of the device layers may be formed using a solution processing method. For example, the perovskite light-absorber layer 20 may be deposited from a precursor solution using any a solution processing method selected from a list of spin-coating, knife coating, slit-continuous coating, and spray-coating.

An exemplary method 100 of manufacturing the perovskite solar cell 10 will now be described with reference to Fig. 3, which is a flowchart outlining the constituent method steps 102 to 114.

5 The method 100 commences with step 102 which comprises providing a substrate 26 and depositing a negative electrode 22 (e.g. a first electrode) on a receiving surface of the substrate 26. The negative electrode 22 comprises a transparent conductive oxide (e.g. fluorine-doped tin oxide, FTO) which is formed by a plasma-based deposition process (e.g. reactive magnetron sputtering).

10 A second method step 104 involves depositing an electron-transport layer 16 onto the substrate 26 so that the negative electrode 22 is interposed between the electron-transport layer 16 and the substrate 26. The electron-transport layer 16 comprises an n-type (e.g. negatively doped) semiconductor material (e.g. TiO_2), which is deposited using a solution processing method. For example, the electron-transport layer 16 may be formed by spin
15 coating a TiO_2 precursor solution onto a receiving surface of the substrate 26 (e.g. an exposed surface of the negative electrode 22) before then annealing the precursor solution, as will be understood by the skilled person.

20 A third method step 106 involves forming a light-absorber layer 20 on the substrate 26 such that the electron-transport layer 16 and the negative electrode 22 are interposed between the light-absorber layer 20 and the substrate 26. The light-absorber layer comprises a perovskite material, as described above, and the method step 106 comprises coating a perovskite precursor solution onto a receiving surface of the substrate 26 (e.g. an exposed surface of the electron-transport layer 16) and then curing the precursor solution to form the light-absorber
25 layer 20.

The light-absorber layer 20 is arranged in direct physical contact with the electron-transport layer 16, which is interposed between the light-absorber layer and the substrate. Furthermore, the light-absorber layer 20 is electrically connected to the negative electrode 22 (via the
30 electron-transport layer 16), which is also interposed between the light-absorber layer 20 and the substrate 26.

Method step 108 comprises passivating the perovskite material of the light-absorber layer 20 with a passivating medium comprising boron trifluoride (e.g. a first passivation treatment). More
35 specifically, the method step 108 comprises directing a flow of gas comprising boron trifluoride towards the substrate 26 and thus the light-absorber layer 20. According to an exemplary

arrangement, the method step 108 comprises arranging the partially fabricated solar cell 10 (as manufactured according to method steps 102 to 106) in the passivation chamber 32 of the apparatus 30. A flow of gas (e.g. a first gas mixture) is directed into the passivation chamber 32 by controlling the inflow of nitrogen and boron trifluoride gas using the gas flow control device 38. The gas flow into the passivation chamber 32 causes diffusion of boron trifluoride into the light-absorber layer 20, which passivates and stabilises the perovskite material. Whilst the method illustrated in Fig. 3 comprises passivating the light-absorber layer by directing the flow of gas towards the perovskite material subsequently to the step of forming the perovskite material, it can be appreciated that in alternative methods according to the present disclosure, the step of passivating the light-absorber layer may be conducted by directing the flow of gas towards the substrate prior to, or simultaneously with, the step of forming the perovskite material.

The pressure in the passivating chamber 32 during the step of passivating the perovskite material (e.g. the pressure of the first gas mixture comprising boron trifluoride in the passivating chamber 32) is between 10^{-4} mbar and 10^{-6} mbar.

The volume concentration of boron trifluoride gas is between 0.1% to 10%. The remaining volume concentration of the gas flow is nitrogen gas, which acts as an inert carrier gas. The first passivation treatment ends when the gas flow into the passivation chamber 32 is stopped, and the solar cell 10 is ejected from the passivation chamber 32 (e.g. by the transport mechanism 48 of the apparatus 30). The introduction of the gaseous boron trifluoride into the passivation chamber 32 causes passivation of the perovskite material in the light-absorber layer 20, which thereby improves the performance of the solar cell 10.

According to a fifth method step 110, a hole-transport layer 18 is deposited onto the substrate 26 so that the light-absorber layer 20 is interposed between the hole-transport layer 18 and the substrate 26. Accordingly, the light-absorber layer 20 is configured to be in direct physical contact with the hole-transport layer 18, which is arranged on top of the light-absorber layer 20. The hole-transport layer 18 comprises a p-type (i.e. positively doped) semiconductor material (e.g. Spiro-OMeTAD), which is deposited using a solution processing method. For example, the electron-transport layer 16 may be formed by spin coating a Spiro-OMeTAD precursor solution onto a receiving surface of the substrate 26 (e.g. an exposed surface of the light-absorber layer 20), as will be understood by the skilled person.

A sixth method step 112 involves passivating the p-type semiconductor material of the hole-transport layer 18 with a passivating medium comprising boron trifluoride and ammonia gas (e.g. a second passivation treatment). According to an exemplary arrangement, method step 112 comprises directing a flow of gas comprising boron trifluoride gas and ammonia gas
5 towards the substrate 26. In particular, the partially fabricated solar cell 10 (as manufactured according to method steps 102 to 110) is moved into the passivation chamber 32 of the apparatus 30. A flow of gas (e.g. a second gas mixture) is directed into the passivation chamber 32 by controlling the inflow of nitrogen gas, boron trifluoride gas and ammonia gas using the gas flow control device 38. The gas flow into the passivation chamber 32 causes
10 diffusion of boron trifluoride and ammonia into the hole-transport layer 18, which passivates and stabilises the p-type semiconductor material. Whilst the method illustrated in Fig. 3 comprises passivating the hole-transport layer by directing the flow of gas towards the p-doped semiconductor material subsequently to the step of forming the p-doped semiconductor material, it can be appreciated that in alternative methods according to the present disclosure,
15 the step of passivating the hole-transport layer may be conducted by directing the flow of gas towards the substrate prior to, or simultaneously with, the step of forming the p-doped semiconductor material.

The pressure in the passivating chamber during the step of passivating the perovskite material
20 (e.g. the pressure of the second gas mixture comprising boron trifluoride in the passivating chamber) is between 10^{-4} mbar and 10^{-6} mbar.

The volume concentration of boron trifluoride gas is between 0.1% and 10%. The volume concentration of ammonia gas is between 0.1% and 10%. The remaining volume concentration
25 of the gas flow is nitrogen gas. On combining with ammonia gas, the boron trifluoride gas molecules form a Lewis adduct ($\text{NH}_3\cdot\text{BF}_3$) which can act as zwitterion to passivate both anionic and cationic defects in the perovskite material. The zwitterions also act as passivating species in hole-transport layer 18 to facilitate improved extraction of charge carriers from the solar cell 10 e.g. because fewer charge carriers are being trapped by defects in the hole-transport layer. The second passivation treatment ends when the gas flow into the passivation chamber 32 is stopped, and the solar cell 10 is removed from the passivation chamber 32.
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The method 100 concludes with method step 114, which comprises forming a positive electrode 24 (e.g. a second electrode) on the hole-transport layer 18. The positive electrode
35 24 is deposited on a receiving surface of the substrate 26 such that at least the light-absorber layer 20 and the hole-transport layer 18 are interposed between the positive electrode 24 and

the substrate 26. Accordingly, the positive electrode 24 is arranged in direct physical contact with the hole-transport layer 18 and the light-absorber layer 20 is electrically connected to the positive electrode 24, via the hole-transport layer 18. The positive electrode 24 comprises a metal (e.g. gold, Au) which is deposited by a thermal evaporation process.

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According to the exemplary method 100, the perovskite material of the light-absorber layer 20 is subjected to the first passivation treatment (e.g. using the first gas mixture, comprising boron trifluoride and nitrogen gases) and the hole-transport layer 18 is passivated with the second passivation treatment (e.g. using the second gas mixture, comprising boron trifluoride, ammonia and nitrogen gases). However, it will be appreciated that in alternative exemplary methods, the first passivation treatment may be used to passivate the hole-transport layer 18 and the second passivation treatment may be used to passivate the light-absorber layer 20. Alternatively, the method may comprise performing only a single passivation treatment on at least one, or each, of the light-absorber layer 20 and hole-transport layer 18 of the solar cell.

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It will be understood that the invention is not limited to the embodiments above described and various modifications and improvements can be made without departing from the concepts described herein. Except where mutually exclusive, any of the features may be employed separately or in combination with any other features and the disclosure extends to and includes all combinations and sub-combinations of one or more features described herein.

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CLAIMS

1. A method of manufacturing a perovskite solar cell, the solar cell comprising a light-absorber layer comprising a perovskite material and a hole-transport layer comprising a p-type doped semiconductor material, wherein the method comprises:
- 5 forming the perovskite material on a substrate to define the light-absorber layer;
forming the p-type doped semiconductor material on the substrate to define the hole-transport layer; and
passivating one or more layers of the solar cell with a passivating medium comprising boron trifluoride, the one or more layers selected from the group consisting of: the light-absorber layer and the hole-transport layer;
- 10 wherein the step of passivating the one or more layers comprises directing a flow of gas comprising boron trifluoride towards said layers or the substrate said layers are to be formed on.
- 15 2. The method according to claim 1, wherein the method comprises passivating the light-absorber layer by directing the flow of gas comprising boron trifluoride towards the perovskite material simultaneously with and/or subsequently to the step of forming the perovskite material to define the light-absorber element.
- 20 3. The method according to claim 1 or claim 2, wherein the method comprises passivating the light-absorber layer by directing the flow of gas comprising boron trifluoride towards the substrate prior to the step of forming the perovskite material to define the light-absorber element.
- 25 4. The method according to any one of claims 1 to 3, wherein:
the step of passivating one or more layers of the solar cell is carried out in a passivation chamber; and
the pressure in the passivating chamber during the step of passivating the one or more layers of the solar cell is between 10^{-4} mbar and 10^{-6} mbar.
- 30 5. The method according to any one of claims 1 to 4, wherein the percentage concentration by volume of boron trifluoride gas in the flow of gas is between 0.1% and 10%.
- 35 6. The method according to any one of the preceding claims, wherein the flow of gas further comprises ammonia gas.

7. The method according to claim 6, wherein the percentage concentration by volume of ammonia gas in the flow of gas is between 0.1% and 10%.
- 5 8. The method according to any one of the preceding claims, wherein the remainder of the gas consists of chemically inert gas.
9. The method according to claim 8, wherein the chemically inert gas comprises nitrogen.
- 10 10. The method according to any one of the preceding claims, wherein the step of forming the perovskite material and/or the step of forming the p-type doped semiconductor material comprises a vapour deposition process which is selected from the group consisting of: chemical vapour deposition, and plasma-enhanced chemical vapour deposition.
- 15 11. The method according to any one of claims 1 to 9, wherein the step of forming the perovskite material and/or the step of forming the p-type doped semiconductor material comprises a solution deposition process which is selected from the group consisting of: doctor-blade coating, slot-die coating, dip-coating, spray-coating and spin coating.
- 20 12. The method according to any one of the preceding claims, wherein the step of forming the perovskite material comprises forming a material which has a general formula of ABX_3 ;
wherein A is one or more of: an organic monovalent cation including one or more of MA ($CH_3NH_3^+$), FA [$HC(NH_2)_2^+$], EA ($CH_2CH_3NH_3^+$); or an inorganic cation including one or more of Cs^+ and Rb^+ ;
25 wherein B is a transition metal divalent cation including one or more of Pb^{2+} and Sn^{2+} ;
and
wherein X is a monovalent anion including one or more of Cl^- , Br^- and I^- .
- 30 13. The method according to any one of the preceding claims, wherein the method comprises passivating the hole-transport layer by directing the flow of gas comprising boron trifluoride towards the p-type doped semiconductor material simultaneously with and/or subsequently to the step of forming the p-type doped semiconductor material to define the hole-transport layer.
- 35 14. The method according to any preceding claim, wherein the method comprises passivating the p-type doped semiconductor material by directing the flow of gas comprising boron

trifluoride towards the substrate prior to the step of forming the p-type doped semiconductor material to define the hole-transport layer.

15. A perovskite solar cell obtained or obtainable via the method of any one of claims 1 to 14.
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