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(54) **Title:** PEROVSKITE THIN FILM PRODUCTION METHOD AND OPTOELECTRONIC DEVICE

(57) **Abstract:** The present invention relates to a method of organic-inorganic hybrid perovskite semiconductor production. The present invention allows the formation of planar heterojunctions with extremely small film roughness, which is significant for the fabrication of high-efficiency solar cells and other optoelectronic devices. The method has potential for large-scale and low-cost production of perovskite solar cells via currently mastered industrial systems.

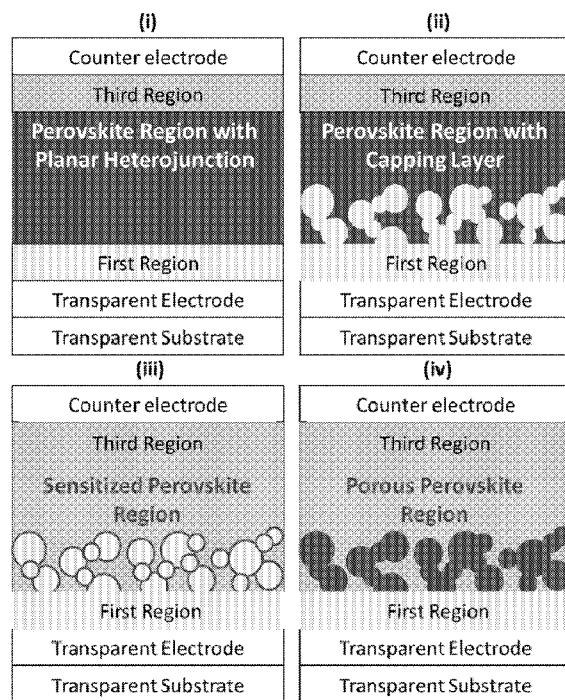


FIG. 1



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DESCRIPTION

PEROVSKITE THIN FILM PRODUCTION METHOD AND OPTOELECTRONIC DEVICE

Field of Invention

The invention relates to processes for producing perovskite layers and processes for producing devices containing perovskite layers. Perovskite layers are useful for light absorbing/emitting optoelectronic devices, transistors, and modulators.

Background to the Invention

Perovskite photovoltaic (PV) technology is one of the most promising solar cell technologies in photovoltaics research due to its high-efficiency and potentially lower production cost of the cells in comparison to other well-known photovoltaic technologies.

Perovskites [Mitzi, D. B. et al., Conducting layered organic-inorganic halides containing <110>-oriented perovskite sheets. *Science*, **1995**, 267, 1473-1476] are an alternative family of semiconductor materials, which have been investigated for device applications [Mitzi D. B. et al., Organic-inorganic electronics. *IBM Journal of Research and Development*, **2001**, 45, 29-45]. Kojima et al. introduced solution-processable hybrid organic-inorganic perovskites of the formula $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) as sensitizers for Dye-Sensitized Solar Cells (DSSCs) reaching a power conversion efficiency (PCE) of 3.8% in conjunction with mesoporous TiO_2 and a iodide/triiodide based liquid electrolyte [Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.* **2009**, 131, 6050-6051]. Im et al. later improved the PCE to 6.5% by optimizing the composition of the redox electrolyte [Im, J.-H. et al. 6.5% efficient perovskite quantum-dot-sensitized solar cell. *Nanoscale* **2011**, 3, 4088-4093]. In both cases, the photovoltaic devices suffered from poor stability due to the rapid dissolution of the perovskite in the liquid electrolyte. This problem could be overcome by using a solid-state configuration, employing spiro-OMeTAD as a hole transporter. In this manner Kim et al. achieved a PCE of

9% [Kim, H.-S. et al. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Sci. Rep.* **2012**, 2, 591]. At the same time, Lee et al. showed that such a device works even better when the semiconducting mesoporous TiO₂ film was replaced by an insulating Al₂O₃ scaffold, indicating rapid electron transport through the perovskite phase [Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science* **2012**, 338, 643-647]. While reaching an impressive PCE of 10.9 % with their champion cell, Lee et al. reported very poor reproducibility and a large spread of photovoltaic device performance. Since the publication of these pioneering studies, several investigations have followed up on this concept [Etgar, L. et al. Mesoscopic CH₃NH₃PbI₃/TiO₂ heterojunction solar cells. *J Am. Chem. Soc.* **2012**, 134, 17396-17399; Im, J.-H.; Chung, J.; Kim, S.-J.; Park, N.-G. Synthesis, structure, and photovoltaic property of a nanocrystalline 2H perovskite-type novel sensitizer (CH₃CH₂NH₃)PbI₃. *Nanoscale Res. Lett.* **2012**, 7, 353; Edri, E.; Kirmayer, S.; Cahen, D.; Hodes, G. High open-circuit voltage solar cells based on organic-inorganic lead bromide perovskite. *Phys. Chem. Lett.* **2013**, 4, 897-902; Crossland, E. J. W. et al. Mesoporous TiO₂ single crystals delivering enhanced mobility and optoelectronic device performance. *Nature* **2013**, 495, 215-219; Noh, J. H.; Im, S. H.; Heo, J. H.; Mandai, T. N.; Seok, S. I. Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. *Nano Lett.* **2013**, 13, 1764-1769; Cai, B.; Xing, Y.; Yang, Z.; Zhang, W.-H.; Qiu, J. High performance hybrid solar cells sensitized by organolead halide perovskites. *Energy Environ. Sci.* **2013**, 6, 1480-1485; and Qui, J. et al. All-solid-state hybrid solar cells based on a new organometal halide perovskite sensitizer and one-dimensional TiO₂ nanowire arrays. *Nanoscale* **2013**, 5, 3245-3248]. In all these previous studies, the perovskite solution was prepared from a solution of two precursors, PbX₂ (X = I, Br or Cl) and CH₃NH₃I (methyammonium iodide) in a common solvent, i.e. N,N-dimethylformamide (DMF) or γ -butyrolactone (GBL). However, there is a lack of control of the morphology of the perovskite crystals formed during this type of solution processing, which is most likely the reason for the poor reproducibility of PV cell performance.

In order to reduce pinhole formation in the perovskite layer, methods such as sequential deposition [Burschka, J. et al., Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature*, **2013**, 499, 316-319] and dual source vapor evaporation [Liu, M.; Johnston M. B.; Snaith, H. J. Efficient planar heterojunction perovskite

solar cells by vapour deposition. *Nature*, **2013**, 501, 395-398] methods are proposed. In a typical sequential deposition process, PbI_2 is first spin-coated from a solution in DMF or dimethyl sulfoxide (DMSO) onto the mesoporous titania film and subsequently transformed into the perovskite by dipping into a solution of methylammonium iodide (MAI), typically in isopropanol. Formation of perovskite is instantaneous within the mesoporous host upon contacting of two components. Burschka et al. demonstrated a PCE of 12.9% by this method. However, two major problems were found for sequential deposition on planar substrate: one is incomplete conversion of PbI_2 to perovskite, and the other is uncontrolled perovskite crystal growth as well as surface morphology, thus leading to the poor reproducibility of the perovskite films as well as a large variation of the photovoltaic response. Liu et al. demonstrated a dual source vapor deposition method where PbCl_2 and MAI vapor is deposited onto the substrate at the same time and a PCE figure of 15.4% is achieved. However, this is a high energy-consuming and slow deposition process with respect to the cost-effective and faster solution processing. Chen et al. developed a vapor-assisted solution process (VASP) for the deposition of perovskite absorbing layer [Chen, Q. et al., Planar heterojunction perovskite solar cells via vapor-assisted solution process. *J. Am. Chem. Soc.* **2014**, 136, 622-625; Hao, F. et al., Controllable perovskite crystallization at a gas-solid interface for hole conductor-free solar cells with steady power conversion efficiency over 10%. *J. Am. Chem. Soc.* **2014**, 136, 16411-16419], which can be thought of as a combination of the previously mentioned methods and demonstrated a PCE figure of 12.1%. Most recently, another two-step method is demonstrated where PbI_2 and MAI solutions are spin-cast onto the substrate sequentially [Xiao, Z. et al., Efficient, high yield perovskite photovoltaic devices grown by interdiffusion of solution-processed precursor stacking layers. *Energy Environ. Sci.* **2014**, 7, 2619; Im, J.-H. et al., Growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$ cuboids with controlled size for high-efficiency perovskite solar cells, *Nature Nanotechnology*, **2014**, 9, 927-932]. Xiao et al. demonstrated a PCE of 15.6% by this method. Im et al. showed that it is easier to control $\text{CH}_3\text{NH}_3\text{PbI}_3$ cuboid formation with this method, therefore, two-step spin coating method is expected to be more precise than the two-step dipping method especially for planar heterojunction devices.

The present invention addresses the disadvantages of optoelectronic devices produced by current methods such as low reproducibility, limited substrate choice, and inapplicability to large area. Devices comprising perovskite layer processed from a solution of two precursors lack control of surface morphology and reproducibility. Two-step dipping method works better with devices with a mesoporous TiO_2 or Alumina scaffold but performs poorly with

planar heterojunction devices. Two-step spin coating method is more advantageous in terms of substrate choice but difficult to adapt to large area substrates due to the spin coating processes involved. VASP seems to address these issues; however, it requires synthesis of large amounts of MAI, which brings forward an additional cost for large scale production.

This invention seeks to provide perovskite solar cells with high-efficiency and large area that can be prepared rapidly in an efficient and reproducible way, using readily available low-cost materials, using a short manufacturing procedure based on industrially known manufacturing steps.

Summary of the Invention

We report a new sequential deposition technique to produce organic-inorganic perovskite films.

In an aspect, the invention provides methods comprising: a step of applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts; and a step of applying and/or depositing one or more acids and amines/amine derivatives in vapor form either sequentially or simultaneously.

The invention provides methods comprising the steps of:

- a) applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts; and
- b) applying and/or depositing one or more acids in vapor form; and
- c) applying and/or depositing one or more amines/amine derivatives in vapor form; and
- d) annealing the existing film

wherein steps a), b), c) and d) may be conducted in any order, either sequentially or simultaneously.

In an aspect, the invention provides a method for producing a nanocrystalline organic-inorganic perovskite layer, the method comprising the steps a), b), c), and d) of the invention.

In an aspect, the invention provides a method for applying and/or producing a perovskite layer on a surface and/or layer, the method comprising the steps a), b), c), and d) of the invention.

In an aspect, the invention provides a method for producing an optoelectronic device, the method comprising the steps a), b), c), and d) of the invention.

Accordingly, the invention provides an optoelectronic device comprising a photoactive region, in which photoactive region comprises:

- an n-type region comprising at least one n-type layer;
- a p-type region comprising at least one p-type layer;
- and, disposed between the n-type region and the p-type region:
a layer of a perovskite semiconductor produced by the method comprising the steps a), b), c), and d) of the invention.

Typically, the optoelectronic device is a photovoltaic device. Alternatively, the optoelectronic device may be other than a photovoltaic device. The optoelectronic device may for instance be a light-emitting device, transistor, or a modulator.

In another aspect, the invention provides a process for a photoactive region which comprises:

- (i) providing a first region;
- (ii) disposing a second region on the first region, which comprises a layer of a perovskite semiconductor produced by the method comprising the steps a), b), c), and d) of the invention as described previously,
- (iii) disposing a third region on the second region,

wherein:

- the first region is an n-type region comprising at least one n-type layer and the third region is a p-type region comprising at least one p-type layer; or
- the first region is a p-type region comprising at least one p-type layer and the third region is an n-type region comprising at least one n-type layer.

Perovskite region (second region) can form various junctions with the first and third regions:

- (i) the perovskite region forms a planar heterojunction with the first and third regions.
- (ii) there is a porous scaffold which infiltrates into the perovskite region stretching from the first region. The porous scaffold may or may not be made of the same material as the first

region. The perovskite region involves a capping layer on top of the porous scaffold, which forms a planar heterojunction with the third region.

(iii) there is a porous scaffold which infiltrates into the perovskite region stretching from the first region. The porous scaffold may or may not be made of the same material as the first region. A thin perovskite layer is sensitized on the porous scaffold. Third region infiltrates into said sensitized perovskite layer.

(iv) there is a porous perovskite region on top of the first region. Third region infiltrates into said porous perovskite region.

Typically, the process of the invention is to produce a photovoltaic device comprising said photoactive region. Alternatively, the process may be used to produce an optoelectronic device other than a photovoltaic device, in which optoelectronic device comprises said photoactive region. The process may for instance be used to produce a light-emitting device, transistor, or modulator comprising said photoactive region.

In some embodiments, the optoelectronic device comprises:

- (1) transparent carrier substrate with transparent electrode
- (2) a first region with n/p-type layer;
- (3) disposing a second region on the first region, which second region comprises:
 - a) applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts; and
 - b) applying and/or depositing one or more acids in vapor form; and
 - c) applying and/or depositing one or more amines/amine derivatives in vapor form; and
 - d) annealing the existing filmwherein steps a), b), c), and d) may be conducted in any order, either sequentially or simultaneously.
- (4) disposing a third region with p/n-type layer on the second region,
- (5) deposition of a counter electrode.

In some embodiments, the first region is n-type and the third region is p-type while in other embodiments the first region is p-type and the third region is n-type.

The invention further provides an optoelectronic device, which is obtainable by the process of the invention for producing an optoelectronic device. Typically, the optoelectronic device is a

photovoltaic device. Alternatively, the optoelectronic device may be other than a photovoltaic device. The optoelectronic device may for instance be a light-emitting device, a transistor, or a modulator.

Brief Description of the Figures

Figure 1. Perovskite region (second region) can form various junctions with the first and third regions:

- (i) the perovskite region forms a planar heterojunction with first and third regions.
- (ii) there is a porous scaffold which infiltrates into the perovskite region stretching from the first region. The porous scaffold may or may not be made of the same material as the first region. The perovskite region involves a capping layer on top of the porous scaffold which forms a planar heterojunction with the third region.
- (iii) there is a porous scaffold which infiltrates into the perovskite region stretching from the first region. The porous scaffold may or may not be made of the same material as the first region. A thin perovskite layer is sensitized on the porous scaffold. Third region infiltrates into said sensitized perovskite layer.
- (iv) there is a porous perovskite region on top of the first region. Third region infiltrates into said porous perovskite region.

Figure 2. An exemplary device architecture. Glass/ITO substrate comprises the transparent carrier substrate and the transparent electrode and acts as a support layer for the device. PEDOT:PSS acts as the first region, which is p-type. Perovskite layer is deposited on top of the first region by the methods described elsewhere in this specification. PCBM acts as the third region, which is n-type. The third region may comprise additional layers such as BCP and C60 layers. Aluminum acts as the counter electrode. Prior to characterization, the device is encapsulated via resin and the encapsulation glass acts as the top support.

Figure 3. The current density-voltage (J-V) curve of an exemplary device. The best device gave a PCE of 9.59% with an open circuit voltage (V_{oc}) of 0.77 V, a short-circuit density of (J_{sc}) of -38.1 mA/cm^2 , and FF of 0.33.

Figure 4. Optical absorbance of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ film produced by the method of the invention. The extrapolated onset absorption of perovskite film gives a band gap of 1.57 eV, in agreement with the literature reports. The relatively high intensity of peaks at ca. 750 nm and ca. 500 nm indicates good formation of perovskite crystals.

Figure 5. Atomic Force Microscopy image of (a) a neat PbI_2 film and (b) a $\text{CH}_3\text{NH}_3\text{PbI}_3$ film produced by the method of the invention. The surface roughness (R_q) of the film is mainly limited by the predeposited PbI_2 film. The R_q value for the PbI_2 film is 6.5 nm whereas R_q value for the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film is 8.5 nm.

Figure 6. X-Ray Diffraction spectrum of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ film produced by the method of the invention. The major diffraction peak of the PbI_2 film was found at 12.8° . $\text{CH}_3\text{NH}_3\text{PbI}_3$ film possesses peaks that can be attributed to either $\text{CH}_3\text{NH}_3\text{PbI}_3$ or PbI_2 crystals. The diffraction peaks of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal at 14.3° , 28.6° , and 43.3° can be assigned to (110), (220), and (330) planes, respectively. The comparison of (110) plane peak of $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal with respect to strong diffraction plane peak of PbI_2 crystal can be used to evaluate the extent of perovskite film formation. In this regard, it can be said that there is a good level of conversion of PbI_2 crystals to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal. The presence of PbI_2 crystal diffraction peaks indicate the perovskite formation is not complete and may explain the relatively poor fill factors of the devices obtained from these films compared to state of art. The device performances can be further optimized by increasing the conversion of PbI_2 crystals to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals.

Detailed Description of the Invention

The present invention encompasses the formation of an organic-inorganic perovskite layer, which is preferably provided on a surface and/or on a layer.

The term "perovskite", as used herein, refers to a material with the same type of crystal structure as calcium titanium oxide (CaTiO_3), known as the perovskite structure, or ABX_3 , which has a three-dimensional network of corner-sharing BX_6 octahedra. The B component in the ABX_3 structure is a metal cation that can adopt an octahedral coordination of X anions. The A cation is situated in the 12-fold coordinated holes between the BX_6 octahedra and is most commonly inorganic. By replacing the inorganic cation with an organic cation, an

organic-inorganic hybrid perovskite can be formed. A_2BX_4 , ABX_4 and A_3BX_5 perovskites are also considered members of his family. Other types of organic-inorganic hybrid semiconductors may include crystal structures adopting the formula such as AB_2X_6 and A_2BX_6 . In the perovskites according to the present invention, the A component in the ABX_3 structure is a monovalent or divalent organic ammonium cation, such as monovalent organic ammonium cation D or divalent organic ammonium cation E as defined below in this specification; the B component in the ABX_3 structure is a divalent or trivalent metal cation, such as divalent metal cation M or trivalent metal cation N as defined below in this specification; and the X component in the ABX_3 structure is an anion.

When the perovskite comprise more than one A cation, the different A cations may be distributed over the A sites in an ordered or disordered way. When the perovskite comprises more than one B cation, the different B cations may be distributed over the B sites in an ordered or disordered way. When the perovskite comprise more than one X anion, the different X anions may be distributed over the X sites in an ordered or disordered way.

The present invention also provides a process for an optoelectronic device comprising a photoactive region involving:

- an n-type region comprising at least one n-type layer;
- a p-type region comprising at least one p-type layer;
- and, disposed between the n-type region and the p-type region: a layer of a perovskite semiconductor which is produced by:

- a) applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts; and
- b) applying and/or depositing one or more acids in vapor form; and
- c) applying and/or depositing one or more amines/amine derivatives in vapor form; and
- d) annealing the existing film

wherein steps a), b), c), and d) may be conducted in any order, either sequentially or simultaneously.

The term "acid", as used herein, refers to an inorganic compound with the formula HX where X is anion of a group 7 element, i.e., of a halogen, or an organic anion such as NCS^- , CN^- , CH_3COO^- , and NCO^- . Preferably, HX is a hydrogen halide, i.e., hydrogen fluoride, hydrogen chloride, hydrogen bromide, or hydrogen iodide. More preferably HX is hydrogen iodide.

The term "amines/amine derivative", as used herein, refers to an organic compound with one or more amine groups. Organic compound is preferably in the form of R^1NH_2 , R^1R^2NH , $R^1R^2R^3N$, $R^1(NH_2)_2$. Preferred examples of amines would be: Ethylamine, methylamine, dimethylamine, trimethylamine, formamidine, ethylenediamine.

The term "photoactive region", as used herein, refers to a region in the optoelectronic device which (i) absorbs light, which may then generate free charge carriers; or (ii) accepts charge, both electrons and holes, which may subsequently recombine and emit light; or (iii) changes electrical conductivity by applied bias; or (iv) changes the amplitude of the carrier signal in accordance to the instantaneous amplitude of the modulating signal.

The term "semiconductor" as used herein refers to a material with electrical conductivity intermediate in magnitude between that of a conductor and a dielectric. A semiconductor may be an n-type semiconductor, a p-type semiconductor, or an intrinsic semiconductor.

As used herein, the term "n-type region", refers to a region of one or more electron-transporting materials. It may additionally comprise hole-blocking materials, bulk heterojunctions and protective layers. The term "electron-transporting layer" refers to a layer of an electron-transporting material. An "electron-transporting material" is any material or composition wherein charges are transported mainly by electron movement across said material or composition. An electron-transporting material could be a single electron-transporting compound or elemental material, or a mixture of two or more electron-transporting compounds or elemental materials. An electron-transporting compound or elemental material may be undoped or doped with one or more dopant elements. Similarly, the term "hole-blocking layer" refers to a layer of a hole-blocking material. A "hole-blocking material" is any material or composition wherein electron movement is allowed and hole movement is partially or fully blocked across said material or composition. A hole-blocking material could be a single hole-blocking compound or elemental material, or a mixture of two or more hole-blocking compounds or elemental materials. A hole-blocking compound or elemental material may be undoped or doped with one or more dopant elements. Bulk heterojunction and protective layers are defined elsewhere in this specification.

As used herein, the term "p-type region", refers to a region of one or more hole-transporting materials. It may additionally comprise electron-blocking materials, bulk heterojunctions and protective layers. The term "hole-transporting layer" refers to a layer of a hole-transporting material. A "hole-transporting material" is any material or composition wherein charges are transported mainly by hole movement across said material or composition. A hole-transporting material could be a single hole-transporting compound or elemental material, or a mixture of two or more hole-transporting compounds or elemental materials. A hole-transporting compound or elemental material may be undoped or doped with one or more dopant elements. Similarly, the term "electron-blocking layer" refers to a layer of an electron-blocking material. An "electron-blocking material" is any material or composition wherein hole movement is allowed and electron movement is partially or fully blocked across said material or composition. An electron-blocking material could be a single electron-blocking compound or elemental material, or a mixture of two or more electron-blocking compounds or elemental materials. An electron-blocking compound or elemental material may be undoped or doped with one or more dopant elements. Bulk heterojunction and protective layers are defined elsewhere in this specification.

As used herein, the term "bulk heterojunction", refers to a layer consisting of a nanoscale blend of electron donor and electron acceptor materials. An electron donor is a chemical entity that donates electrons to another compound. An electron acceptor is a chemical entity that accepts electrons transferred to it from another compound. An electron acceptor can be envisioned as a hole donor. Bulk heterojunction layer absorbs photons and generates electron and hole carriers. A typical bulk heterojunction layer comprises organic electron-transporting materials and organic hole-transporting materials such as Poly-(3-hexylthiophene-2,5-diyl) (P3HT) and Phenyl-C61-butyric acid methyl ester (PCBM).

As used herein, the term "protective layer", refers to a layer of semiconducting or thin dielectric layer which allows charge transport. It comprises a conformal coating which is compact enough to avoid short circuits and pin holes between the layers in which said protective layer is placed. The protective layer preferably comprises a metal oxide. In particular, the protective layer may comprise or consist essentially of a material selected from Mg-oxide, Hf-oxide, Ga-oxide, In-oxide, Nb-oxide, Ti-oxide, Ta-oxide, Y -oxide and Zr-oxide. Ga-oxide is a preferred material for said protective layer. The protective layer preferably has a thickness of not more than 5 nm, preferably 4 nm or less, even more

preferably 3 nm or less, and most preferably 2 nm or less. Said metal "protective layer" is preferably a "buffer layer" and provided by atomic layer deposition (ALD). For example, 2 to 7 layers are deposited by ALD so as to provide said protective layer. Accordingly, said protective layer is preferably a metal oxide multilayer.

The invention provides a process for a photoactive region which comprises:

- (i) providing a first region;
- (ii) disposing a second region on the first region, which second region comprises a layer of a perovskite semiconductor produced by the method comprising:
 - a) applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts; and
 - b) applying and/or depositing one or more acids in vapor form; and
 - c) applying and/or depositing one or more amines/amine derivatives in vapor form; and
 - d) annealing the existing filmwherein steps a), b), c), and d) may be conducted in any order, either sequentially or simultaneously.
- (iii) disposing a third region on the second region, wherein:
 - the first region is an n-type region comprising at least one n-type layer and the third region is a p-type region comprising at least one p-type layer;
 - or the first region is a p-type region comprising at least one p-type layer and the third region is an n-type region comprising at least one n-type layer.

Perovskite region (second region) can form various junctions with the first and third regions:

- (i) the perovskite region forms a planar heterojunction with the first and third regions.
- (ii) there is a porous scaffold which infiltrates into the perovskite region stretching from the first region. The porous scaffold may or may not be made of the same material as the first region. The perovskite region involves a capping layer on top of the porous scaffold which forms a planar heterojunction with the third region
- (iii) there is a porous scaffold which infiltrates into the perovskite region stretching from the first region. The porous scaffold may or may not be made of the same material as the first region. A thin perovskite layer is sensitized on the porous scaffold. Third region infiltrates into said sensitized perovskite layer.

(iv) there is a porous perovskite region on top of the first region. Third region infiltrates into said porous perovskite region as depicted in Figure 1.

According to a preferred embodiment, perovskite region (second region) forms the following junctions with the first and third regions:

- (i) the perovskite region forms a planar heterojunction with the first and third regions.
- (ii) there is a porous scaffold which infiltrates into the perovskite region stretching from the first region. The porous scaffold may or may not be made of the same material as the first region. The perovskite region involves a capping layer on top of the porous scaffold which forms a planar heterojunction with the third region

In some embodiments, the optoelectronic device comprises:

- (1) transparent carrier substrate with transparent electrode
- (2) a first region with n/p-type layer;
- (3) disposing a second region on the first region, which second region comprises:
 - a) applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts; and
 - b) applying and/or depositing one or more acids in vapor form; and
 - c) applying and/or depositing one or more amines/amine derivatives in vapor form; and
 - d) annealing the existing filmwherein steps a), b), c), and d) may be conducted in any order, either sequentially or simultaneously.
- (4) disposing a third region with p/n-type layer on the second region,
- (5) deposition of a counter electrode.

In some embodiments, the first region is n-type and the third region is p-type while in other embodiments the first region is p-type and the third region is n-type.

According to an embodiment, the optoelectronic device of the invention preferably comprises a carrier substrate. The carrier substrate preferably provides the physical support of the device. Furthermore, the carrier substrate preferably provides a protection with respect to physical damage and thus delimits the optoelectronic device with respect to the outside. According to an embodiment, the optoelectronic device may be constructed by applying the different layers in a sequence of steps, one after the other, onto the carrier substrate. The

carrier substrate may thus also serve as a starting support for the fabrication of the optoelectronic device.

The carrier substrate is preferably transparent, so as to let light pass through the optoelectronic device. "Transparent" means transparent to at least a part, preferably a major part of the visible light. Preferably, the carrier substrate is substantially transparent to all wavelengths or types of visible light. Furthermore, the carrier substrate may be transparent to non-visible light, such as ultraviolet and infrared radiation, for example.

Conveniently, and in accordance with a preferred embodiment of the invention, a current collector electrode is provided. The electrode layer is preferably transparent. It can replace or contain the carrier substrate as in the case of conductive glass or conductive plastic. Examples of transparent electrodes are indium doped tin oxide (ITO), fluorine doped tin-oxide (FTO), ZnO-Ga₂O₃, ZnO-Al₂O₃, tin-oxide, antimony doped tin oxide (ATO), SrGeO₃, zinc oxide, silver nanowires, carbon nanotubes, and graphene.

According to a preferred embodiment, the perovskite region (second region) forms a planar heterojunction with the first region. First region can either be n-type or p-type. If the divalent/trivalent metal salt is spin cast from a solvent such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO) or γ -butyrolactone (GBL), it is preferable that the first region should not be soluble by these solvents. Preferred n-type materials are compact TiO_x, ZnO_x films and a preferred p-type layer is PEDOT:PSS.

According to another embodiment, there is a porous scaffold between the first region and the perovskite region (second region) which increases the interaction area. Preferably, there will be a capping layer of the perovskite film into which the porous scaffold does not infiltrate. A preferred scaffold will be made out of titania and/or alumina nanoparticles.

The method of the invention comprises the steps of:

- a) applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts; and
- b) applying and/or depositing one or more acids in vapor form; and
- c) applying and/or depositing one or more amines/amine derivatives in vapor form; and
- d) annealing the existing film

wherein steps a), b), c), and d) may be conducted in any order onto the first region, either sequentially or simultaneously.

According to a preferred embodiment, steps a), b), c), and d) are conducted onto the first region in the following order:

- 1) performing step a), i.e., applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts
- 2) performing step b), i.e., applying and/or depositing one or more acids in vapor form
- 3) performing step c), i.e., applying and/or depositing one or more amines/amine derivatives in vapor form
- 4) performing another step b), i.e., applying and/or depositing one or more acids in vapor form
- 5) performing step d), i.e., annealing the existing film

but the present invention also encompasses, in other embodiments, that step a), b), c), and d) is conducted in any order either sequentially or simultaneously.

According to an embodiment, said one or more divalent or trivalent metal salts in step a) are selected from salts of formula MX_2 or NX_3 wherein:

M is a divalent metal cation selected from the group consisting of Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Cr^{2+} , Pd^{2+} , Cd^{2+} , Ge^{2+} , Sn^{2+} , Pb^{2+} , Eu^{2+} , or Yb^{2+} ;

N is a trivalent metal cation selected from the group of Bi^{3+} and Sb^{3+} ; and X is independently selected from F^- , Cl^- , Br^- , I^- , NCS^- , CN^- , CH_3COO^- , and NCO^- .

Preferably, said metal salt is MX_2 .

According to a preferred embodiment, said divalent or trivalent metal salt, preferably a divalent metal salt, is a metal halide. Preferably, in case two or more different divalent or trivalent metal salts, preferably two or more different divalent metal salts, are used, these are different metal halides.

According to a more preferred embodiment, the metal ion said divalent or trivalent metal salt is Pb^{2+} . According to another preferred embodiment, the halide in said divalent or trivalent metal salt is I^- . According to another preferred embodiment, the divalent or

trivalent metal salt is PbI_2 . According to another preferred embodiment, in case two or more different divalent metal salts, are used, the second salt is SnI_2 .

According to an embodiment, said film comprising said one or more divalent or trivalent metal salt is applied and/or deposited (step a)) by any one or more methods selected from: deposition from solution, deposition from a dispersion, for example, from a colloidal dispersion, deposition by thermal evaporation, deposition by sputtering, electrodeposition, atomic-layer-deposition (ALD), and formation of the metal salt in situ. The latter comprises the possibility of applying and/or depositing the divalent or trivalent metal salt in a two or multi-step process, for example by depositing a precursor onto the surface that is subsequently transformed into the divalent or trivalent metal salt.

Examples of deposition from solution encompass, for example, drop casting, spin-coating, dip-coating, curtain coating, spray-coating, doctor blading, screen printing and ink-jet printing.

According to an embodiment, said film comprising one or more divalent or trivalent metal salt is applied and/or deposited by spin-coating a solution of one or more said divalent or trivalent metal salts, preferably at 2000 rpm or more, preferably 3000 rpm or more. Preferably, said spin-coating takes place for 1 s (second) to 10 minutes, preferably 2 s to 30 s.

The solvent used for the spin-coating may be any solvent that dissolves the one or more divalent or trivalent metal salts. Preferably, when the metal salt is PbI_2 , the solvent is N,N-dimethylformamide (DMF) or γ -butyrolactone (GBL).

Preferably, the concentration of the one or more divalent or trivalent metal salts in the solution used for the spin-coating for obtaining the film comprising the one or more divalent or trivalent metal salt is 50 mg/mL or more, more preferably 250 mg/mL or more.

When more than one divalent metal salts are applied and/or deposited, the two different salts may be applied at the same time. For example, in case of deposition from a solution, the solution may contain different metal salts. Said different metals salts preferably differ with respect to the anion. Accordingly, divalent metals salts MX^{i}_2 and MX^{ii}_2 , or for example divalent metals salts MX^{i}_2 , MX^{ii}_2 and MX^{iii}_2 are deposited at the same time, for example are

present in the same solution, M being a defined metal and X^i , X^{ii} and X^{iii} being different anions selected from the above, preferably different halides. For example, X^i , X^{ii} and X^{iii} are I^- , Cl^- and Br^- , respectively.

According to an embodiment, the method of the invention comprises the steps of applying and/or depositing a film comprising two or more divalent metal salts selected from MX^i_2 , MX^{ii}_2 and MX^{iii}_2 , wherein X^i , X^{ii} and X^{iii} (charge not shown) are each different anions selected from I^- , Cl^- , Br^- , I^- , NCS^- , CN^- , CH_3COO^- , and NCO^- , preferably from I^- , Cl^- , and Br^- .

In accordance with an embodiment, in step a) a mixture of M^iX_2 with $M^{ii}X$ or $M^{iii}X_3$ may be applied, said M^iX_2 and one from $M^{ii}X$ and $M^{iii}X_3$ being preferably applied together/at the same time, for example deposited from the same solution. In this case M^{ii} and M^{iii} represent monovalent or trivalent cations.

In another embodiment, in step a) a mixture of metal salts with identical charges M^iX_2 and $M^{ii}X_2$ may be applied, said M^iX_2 and $M^{ii}X_2$ being preferably applied together/at the same time, for example deposited from the same solution. In this case M^i and M^{ii} represent divalent cations, which would be used to engineer the bandgap of the perovskite semiconductor. Preferably M^{ii} and M^{iii} will be Pb and Sn.

According to a preferred embodiment, between step a) and step b), the carrier substrate with the metal salt film is annealed between 50 °C and 140 °C, more preferably at 70 °C. The duration of annealing is between 0 to 1 hours, preferably between 5 minutes to 30 minutes. When step b) and step c) is conducted after step a), it preferably comprises or consists essentially of the step of exposing or contacting the film comprising the one or more divalent or trivalent metal salts obtained in step a) to the vapor of one or more acids in step b) and the vapor of one or more amines/amine derivatives in step c).

According to an embodiment, said acid is an inorganic compound with the formula HX where X is anion of a group 7 element, i.e., of a halogen, or an organic anion such as NCS^- , CN^- , CH_3COO^- , and NCO^- . Preferably, HX is a hydrogen halide, i.e., hydrogen fluoride, hydrogen chloride, hydrogen bromide, or hydrogen iodide. More preferably HX is hydrogen iodide.

According to an embodiment, said amines/amine derivative is selected from primary, secondary and tertiary amines R^1NH_2 , R^1R^2NH , $R^1R^2R^3N$ and $R^1(NH_2)_2$. Preferably amines/amine derivatives are alkyl amines, more preferably, methylamine and formamidine.

A mixed perovskite is obtained if the film comprising divalent metal salts in step a) comprises MX^i_2 and MX^{ii}_2 , or MX^i_2 , MX^{ii}_2 and MX^{iii}_2 , for example, is exposed to an acid in step b), which may be selected, independently from any one of HX^i , HX^{ii} and HX^{iii} and further exposed to an amine/amine derivative in step c).

Preferably, if the film comprising divalent metal salts comprises MX^i_2 and MX^{ii}_2 , the acid is selected from salts comprising one of the anions contained in the divalent metal salt layer, for example from HX^i or HX^{ii} .

According to an embodiment, the method of the invention comprises the step (e.g. step a)) of applying and/or depositing a film comprising MI_2 and one selected from MCl_2 and MBr_2 . For example, MI_2 and MCl_2 or MI_2 and MBr_2 , respectively, are deposited from the same solution in which they are dissolved. According to an embodiment, the method of the invention comprises the step (e.g. step b)) of applying one or more acids in vapor form, preferably HI vapor, and one or more amines/amine derivatives in vapor form onto the divalent metal halides obtained in the previous step. Preferably, M is Pb and/or amine/amine derivative is methylamine or formamidine.

According to another embodiment, the method of the invention comprises the step (e.g. step a)) of applying and/or depositing a film comprising MCl_2 and one selected from MI_2 and MBr_2 . For example, MCl_2 and MI_2 or MCl_2 and MBr_2 respectively, are deposited from the same solution in which they are dissolved. According to an embodiment, the method of the invention comprises the step (e.g. step b)) of applying one or more acids in vapor form, preferably HI vapor, and one or more amines/amine derivatives in vapor form onto the divalent metal halides obtained in the previous step. Preferably, M is Pb and/or amine/amine derivative is methylamine or formamidine.

According to a preferred embodiment, step c) comprises applying and/or depositing one single and/or one structurally defined amine/amine derivative. However, it is possible to apply/deposit more than one amine/amine derivative in order to enhance crystallization.

Preferably, in the case of a single type of divalent or trivalent metal ion, salt is deposited in step a). If the first amine/amine derivative is methylamine, the second amine/amine derivative is preferably formamidine.

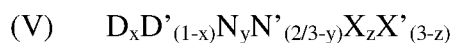
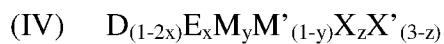
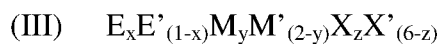
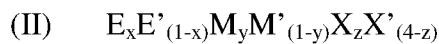
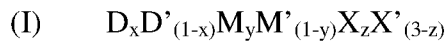
According to an embodiment, vapors of acids and amines/amine derivatives in steps b) and c) can be obtained in (i) direct form; or (ii) from solutions under reduced pressure; or (iii) by heating the said chemicals in a controlled atmosphere. According to an embodiment, in step b) vapor of one or more acids can be applied directly or with a carrier gas onto the divalent or trivalent metal salt from concentrated or dilute acid solutions. Preferably, there is a single type of acid vapor which is HI vapor. Preferably, HI vapor is applied from a concentrated HI solution with a concentration ranging from 48% to 67% in water by mass. Similarly in step c) vapor of one or more amines/amine derivatives can be applied directly or with a carrier gas from concentrated or dilute amine solutions. If the amine/amine derivative is methylamine, preferably the weight percent of amine content is larger than 40% by mass in water or methanol. If the amine/amine derivative is formamidine, preferably it is applied directly in vapor form.

According to an embodiment, step b) and step c) can both be applied in an open chamber or closed chamber, preferably in a closed chamber. According to a preferred embodiment, when step b) and step c) is applied in a closed chamber, the partial vapor pressures and flow rates of the acid vapors and amine/amine derivative vapors can be varied or fixed, preferably they are fixed. According to a preferred embodiment, steps b) and c) can be applied in any order either sequentially or simultaneously when applied in a closed chamber with fixed partial pressures and fixed flow rates for the acid vapors, the amines/amine derivative vapors and the corresponding carrier gases (if any).

According to a preferred embodiment, when step b) and step c) is conducted after step a), they can be applied in any order either sequentially or simultaneously. Preferably, a step b) is conducted first, followed by step c), which is followed by another step b). The duration of each step depends on the vapor pressure and flow rates of the gases involved. According to a preferred embodiment, the duration of the step b) is anywhere between 0 seconds to 10 minutes, more preferably between 5 seconds to 2 minutes and the duration of step c) is anywhere between 0 seconds to 10 minutes, more preferably between 0 seconds to 30 seconds.

According to a preferred embodiment, after vapor deposition of acids and amines/amine derivatives, step d) is applied in which the carrier substrate with the perovskite film is annealed between 60 °C and 180 °C, preferably between 90 °C and 120 °C, and more preferably at 100 °C. The duration of step d) is between 0 and 4 hours, preferably between 30 minutes to 2 hours.

According to an embodiment, the organic-inorganic perovskite material that is used and/or obtained in the previous step preferably comprises a perovskite-structure of any one of formulae (I), (II), (III), (IV), (V) and/or (VI) below:



wherein D is a monovalent organic cation, E is a divalent organic cation, M is a divalent metal cation and N is a trivalent metal cation.

In formulae (V) and (VI) “2/3” means every third metal cation is missing. In this case, the perovskite is metal deficient.

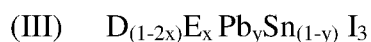
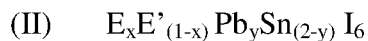
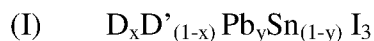
Preferably, M is Sn^{2+} or Pb^{2+} , more preferably Pb^{2+} . N is preferably selected from the group of Bi^{3+} and Sb^{3+} .

In the perovskites of formulae (I) to (VI), any X and X' may be selected independently from F^- , Cl^- , Br^- , I^- , NCS^- , CN^- , CH_3COO^- , and NCO^- . Preferably, X is halogen, preferably X is selected from Br^- or I^- , more preferably X is I^- .

In the perovskites of formulae (I) to (VI), $D_x D'_{(1-x)}$ means different monovalent organic D cations may be distributed over the D sites in an ordered or disordered way; $E_x E'_{(1-x)}$ means different divalent organic E cations may be distributed over the E sites in an ordered or disordered way; $D_{(1-2x)} E_x$ means monovalent D cation and divalent E cation may be distributed over the organic cation sites in an ordered or disordered way. When the perovskite comprises more than one metal cation, $M_y M'_{(1-y)}$ and $M_y M'_{(2-y)}$ means different M cations may be

distributed over the M sites in an ordered or disordered way; $N_yN'_{(2/3-y)}$ means different N cations may be distributed over the N sites in an ordered or disordered way. When the perovskite comprise more than one X anion, $X_zX'_{(3-z)}$, $X_zX'_{(4-z)}$, $X_zX'_{(6-z)}$ means the different X anions may be distributed over the X sites in an ordered or disordered way.

According to a preferred embodiment, said organic-inorganic perovskite layer comprises a perovskite-structure of any one of the formulae

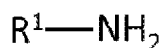


wherein;

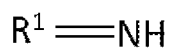
E is preferably $C_2H_4(NH_3)_2^{2+}$ (ethylenediammonium dication), D is preferably $CH_3NH_3^+$ (methyammonium) and D' is an organic cation that enhances perovskite crystallization such as $CH(NH_2)_2^+$ (formamidinium).

According to an embodiment, organic monovalent cation D and organic divalent cation E is originated from the amine/amine derivative evaporated in step c) of the invention. Amines/amine derivatives that can be utilized to have monovalent cation D or D' in the final perovskite structure can be selected independently from one of the compounds below:

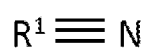
(a)



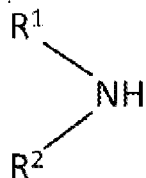
(b)



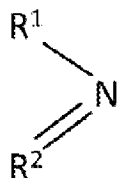
(c)



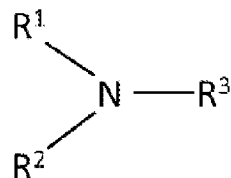
(d)



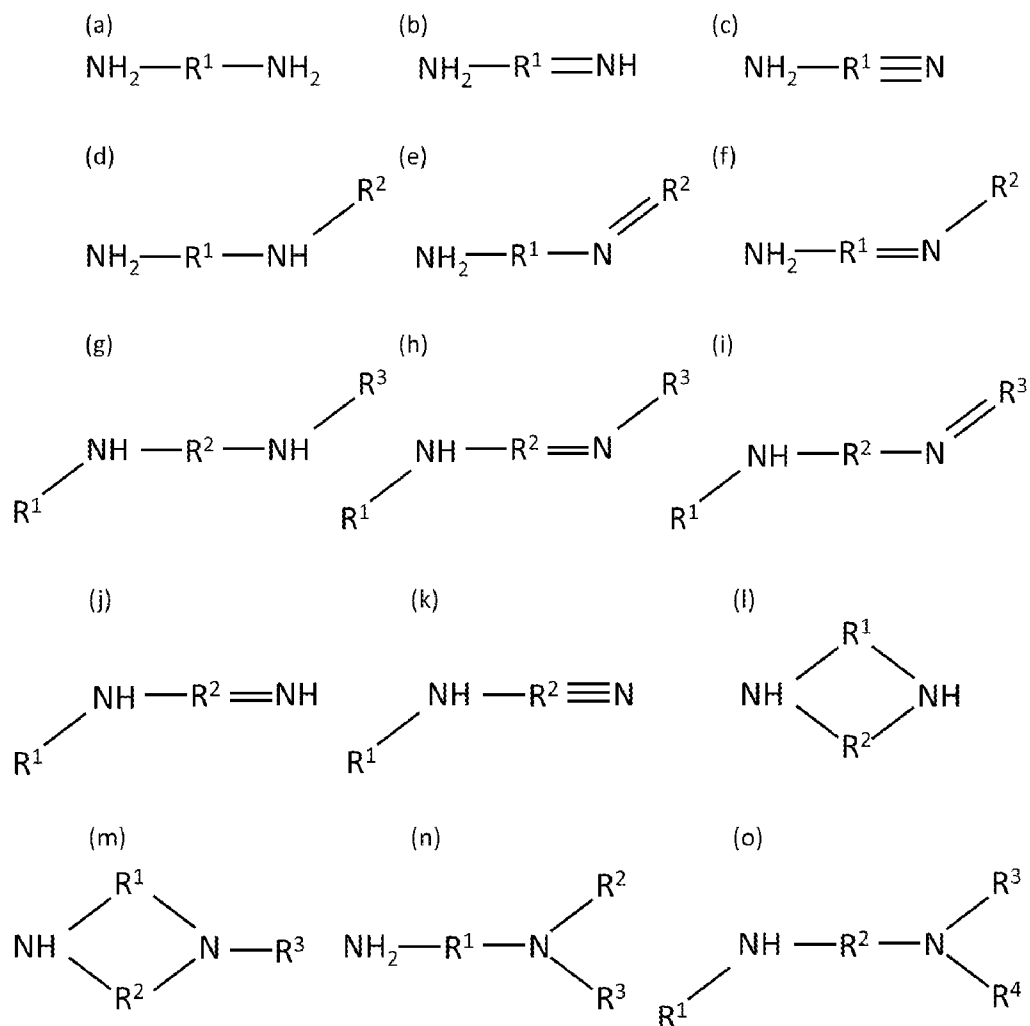
(e)

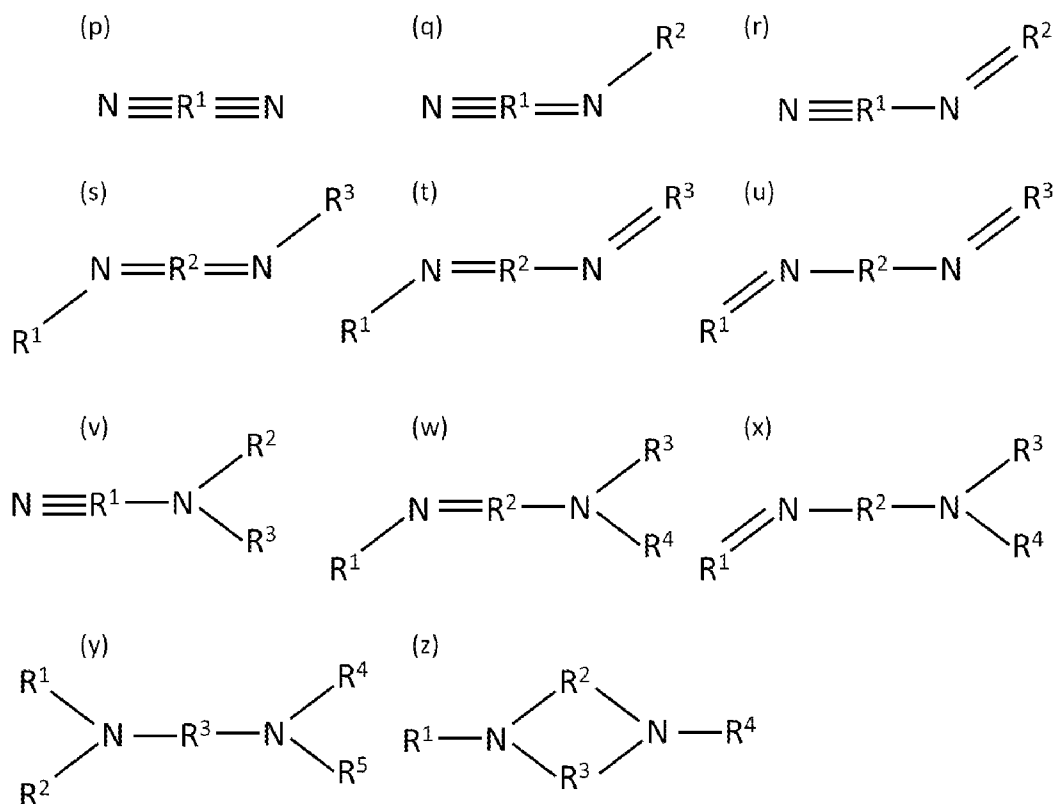


(f)



Amines/amine derivatives that can be utilized to have divalent cation E in the final perovskite structure can be selected independently from one of the compounds below:





wherein, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from from C1-C15 organic substituents comprising from 0 to 15 heteroatoms.

According to an embodiment of said C1-C15 organic substituent any one, several or all hydrogens in said substituent may be replaced by halogen and said organic substituent may comprise up to fifteen (15) N, S or O heteroatoms, and wherein, in any one of the compounds (2) to (8), the two or more of substituents present (R^1 , R^2 , R^3 , R^4 , and R^5 , as applicable) may be covalently connected to each other to form a substituted or unsubstituted ring or ring system. Preferably, in a chain of atoms of said C1-C15 organic substituent, any heteroatom is connected to at least one carbon atom. Preferably, neighboring heteroatoms are absent and/or heteroatom-heteroatom bonds are absent in said C1-C15 organic substituent comprising from 0 to 15 heteroatoms. According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C15 aliphatic and C4 to C15 aromatic or heteroaromatic substituents, wherein any one, several or all hydrogens in said substituent may be replaced by halogen and wherein, in any one of the compounds (2) to (8), the two or more of the

substituents present may be covalently connected to each other to form a substituted or unsubstituted ring or ring system.

According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C8 organic substituents comprising, from 0 to 4 N, S and/or O heteroatom, wherein, independently of said N, S or O heteroatoms, any one, several or all hydrogens in said substituent may be replaced by halogen, and wherein two or more of substituents present on the same cation may be covalently connected to each other to form a substituted or unsubstituted ring or ring system. Preferably, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C8 aliphatic, C4 to C8 heteroaromatic and C6 to C8 aromatic substituents, wherein said heteroaromatic and aromatic substituents may be further substituted.

According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C6 organic substituents comprising, from 0 to 3 N, S and/or O heteroatom, wherein, independently of said N, S or O heteroatoms, any one, several or all hydrogens in said substituent may be replaced by halogen, and wherein two or more of substituents present on the same cation may be covalently connected to each other to form a substituted or unsubstituted ring or ring system. Preferably, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C6 aliphatic, C4 to C6 heteroaromatic and C6 to C8 aromatic substituents, wherein said heteroaromatic and aromatic substituents may be further substituted.

According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected From C1 to C4, preferably C1 to C3 and most preferably C1 to C2 aliphatic substituents wherein any one, several or all hydrogens in said substituent may be replaced by halogen and wherein two or more of substituents present on the same cation may be covalently connected to each other to form a substituted or unsubstituted ring or ring system.

According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C10 alkyl, C2 to C10 alkenyl, C2 to C10 alkynyl, C4 to C10 heteroaryl and C6 to C10 aryl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, wherein said heteroaryl and aryl may be substituted or

unsubstituted, and wherein several or all hydrogens in any one of R^1 , R^2 , R^3 , R^4 , and R^5 may be replaced by halogen.

According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C8 alkyl, C2 to C8 alkenyl, C2 to C8 alkynyl, C4 to C8 heteroaryl and C6 to C8 aryl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, wherein said heteroaryl and aryl may be substituted or unsubstituted, and wherein several or all hydrogens in R^1 , R^2 , R^3 , R^4 , and R^5 may be replaced by halogen.

According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C6 alkyl, C2 to C6 alkenyl, C2 to C6 alkynyl, C4 to C6 heteroaryl and C6 aryl, wherein said alkyl, alkenyl, and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, wherein said heteroaryl and aryl may be substituted or unsubstituted, and wherein several or all hydrogens in R^1 , R^2 , R^3 , R^4 , and R^5 may be replaced by halogen.

According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 and R^5 is independently selected from C1 to C4 alkyl, C2 to C4 alkenyl and C2 to C4 alkynyl, wherein said alkyl, alkenyl and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, and wherein several or all hydrogens in R^1 , R^2 , R^3 , R^4 , and R^5 may be replaced by halogen.

According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C3, preferably C1 to C2 alkyl, C2 to C3, preferably C2 alkenyl and C2 to C3, preferably C2 alkynyl, wherein said alkyl, alkenyl and alkynyl, if they comprise 3 or more carbons, may be linear, branched or cyclic, and wherein several or all hydrogens in R^1 , R^2 , R^3 , R^4 and R^5 may be replaced by halogen.

According to an embodiment, any one of R^1 , R^2 , R^3 , R^4 , and R^5 is independently selected from C1 to C4, more preferably C1 to C3 and even more preferably C1 to C2 alkyl. Most preferably, any one of R^1 , R^2 , R^3 , R^4 , and R^5 are methyl. Again, said alkyl may be completely or partially halogenated.

Concerning the optoelectronic devices of the invention and the methods of producing them, said optoelectronic device comprises a third region that is applied/deposited on top of the

second region which comprises a perovskite region. Said third region can form various junctions with the perovskite region:

- (i) the third region forms a planar heterojunction with a planar perovskite region.
 - (ii) the third region forms a planar heterojunction with the capping layer of a perovskite region.
 - (iii) the third region infiltrates into a sensitized perovskite layer.
 - (iv) the third region infiltrates into said porous perovskite layer.
- as depicted in Figure 1.

According to preferred embodiments, third region forms the following junctions with the perovskite region:

- (i) the third region forms a planar heterojunction with a planar perovskite region.
- (ii) the third region forms a planar heterojunction with the capping layer of a perovskite region.

wherein, the third region forms a planar heterojunction with the second region in both cases.

The quality of the planar heterojunction between the perovskite (second) region and the third region is extremely important because any pinholes or cracks on the perovskite surface degrade device performance significantly. The present invention minimizes the said pinholes and cracks on the final perovskite surface, because the quality of the perovskite film is limited by the quality of the PbI_2 film. Therefore, the present invention allows the fabrication of high-efficiency solar cell with extremely large short circuit current density.

According to a preferred embodiment, the perovskite layer forms a planar heterojunction with the third region. Third region can either be n-type or p-type. Preferred inorganic n-type materials are compact TiO_x , ZnO_x ; preferred inorganic p-type materials are CuNCS , CuI , MoO_3 , WO_3 ; preferred organic n-type materials are fullerene (C_{60}) and Phenyl-C61-butyric acid methyl ester (PCBM); preferred organic p-type materials are Poly(3-hexylthiophene-2,5-diyl) (P3HT) and Spiro-OMeTAD (2,2',7, 7'-tetrakis-N,N-di-p-methoxyphenylamine-9,9'-spirobifluorene) and derivatives of PTAA (poly(triarylamine)) such as Poly[bis(4phenyl) (2,4,6-trimethylphenyl)amine] or (Poly[bis(4-phenyl)(4-butylphenyl)amine]).

It is noted that the term "organic" in expressions "organic n-type material", "organic p-type material", and the like does not exclude the presence of further components. Further components may be selected from (a) one or more dopants, (b) one or more solvents, (c) one or more other additives such as ionic compounds, and (c) combinations of the aforementioned components, for example. In the organic charge transport material, such further components may be present in amounts of 0-30wt.%, 0-20wt.%, 0-10wt.%, most preferably 0-5wt.%.

Examples of ionic compounds that may be present in organic hole transport materials are TBAPF₆, Na CF₃SO₃, Li CF₃SO₃, LiClO₄, and Li[(CF₃SO₂)₂N].

Examples of other compounds that may be present in organic hole transport materials are amines, 4-tertbutylpyridine, 4-nonyl-pyridine, imidazole, N-methyl benzimidazole, for example.

The counter electrode is applied/deposited on top of the third region. The counter electrode may form the outmost layer and thus one of the outer surfaces of the cell. It is also possible that a substrate or support layer is present on one side of counter electrode.

The counter electrode generally comprises a catalytically active material, suitable to provide electrons and/or fill holes towards the inside of the device. The counter electrode may, for example, comprise one or more materials selected from (the group consisting of) Pt, Au, Ni, Cu, Ag, Al, In, Ru, Pd, Rh, Ir, Os, C, conductive polymer, conductive oxide such as indium doped tin oxide (ITO), fluorine doped tin oxide (FTO), ZnO-Ga₂O₃, ZnO-Al₂O₃, tin-oxide, antimony doped tin oxide (ATO), SrGeO₃ combination of two or more of the aforementioned, for example. Conductive polymers may be selected from polymers comprising polyaniline, polypyrrole, polythiophene, polybenzene, polyethylenedioxythiophene, polypropylenedioxythiophene, polyacetylene, and combinations of two or more of the aforementioned, for example. Such conductive polymers may be used as hole-transporting materials as well.

The counter electrode may be applied as is conventional, for example by thermal evaporation of the counter electrode material onto the third region. The counter electrode is preferably connected to a current collector, which is then connected to the external circuit. As detailed with respect to the first side of the device, a conductive support such as conductive glass or plastic may be electrically connected to the counter electrode on the second side.

The solar cell of the invention is preferably a solid state solar cell. The solar cell is preferably (i) planar heterojunction solar cell or (ii) a solar cell comprising a perovskite region with a capping layer.

According to an embodiment of the invention, solar cell exhibits a power conversion efficiency (PCE) of more than 9%, preferably more than 9.5%. PCE is preferably determined as disclosed in the example and under the conditions specified therein. The solar cell preferably exhibits a short circuit current density more than 20 mA/cm^2 , preferably more than 30 mA/cm^2 , and more preferably more than 38 mA/cm^2 .

In the solar cell shown in Figure 2, Glass/ITO substrate comprises the transparent carrier substrate and the transparent electrode. It acts as a support layer for the device. PEDOT:PSS acts as the first region, which is p-type. Perovskite layer is deposited on top of the first region by the methods described elsewhere in this specification. PCBM acts as the third region, which is n-type. The third region may comprise additional n-type layers such C60 and a hole-blocking layer such as Bathocuproine (BCP) layer. Aluminum acts as the counter electrode. Prior to characterization, the device is encapsulated via resin and the encapsulation glass acts as the top support.

In an exemplary embodiment, the invention is based on the deposition of PbI_2 by solution processing on the first region and the subsequent transformation of the PbI_2 into the desired $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite structure by applying/depositing HI and CH_3NH_2 vapor. We find that the reaction occurs within seconds and allows us to have much better control over the perovskite morphology compared to the previously employed routes. The roughness of the perovskite film is limited by the roughness of PbI_2 film because other precursors are applied in vapor form. Another advantage of the method is that it is easily scalable to large area substrates. The use of this new procedure results not only in an excellent reproducibility of photovoltaic device performance, but also enabled us to reach a new record short circuit current density of 38 mA/cm^2 to the best of our knowledge [Ren, Z. et al., Thermal assisted oxygen annealing for high efficiency planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells. *Sci. Rep.* DOI: 10.1038/srep06752]. Considering the extremely high short circuit current density and the small fill factor of 0.33, PCE of 9.6% can easily be improved via further optimization.

The present invention will now be further illustrated by way of an example. This example does not limit the scope of this invention, which is defined by the appended claims.

Example

METHODS SECTION:

Device Fabrication. Perovskite solar cells were fabricated on patterned indium tin oxide (ITO) glasses with a sheet resistance of 10 Ω /sq. The ITO glass was cleaned by sequential ultrasonic treatment in deionized water, acetone, and isopropanol (IPA), and then treated in a bench-top plasma cleaner (PE-50 bench top cleaner, The Plasma Etch, Inc., USA) for 2 min. Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate (PEDOT:PSS) solution (Heraeus Clevious pH 500) was filtered through a 0.45 μ m filter and then spin coated at 4000 rpm for 60 s on the ITO coated glass substrate. Subsequently, the PEDOT:PSS layer was baked at 140 $^{\circ}$ C for 10 min in the air. The PEDOT:PSS coated substrates were then transferred to a N₂ filled glovebox.

PbI₂ is dissolved in N,N-dimethylformamide (DMF) with a concentration of 250 mg/mL. The PbI₂ solution was spun on PEDOT:PSS coated substrate at 3,000 rpm for 20 s and then the resultant film was dried on a hot plate at 70 $^{\circ}$ C for 5 min and left for cooling. The films are exposed to HI vapor (Merck, 67% in water) for 15 seconds and CH₃NH₂ vapor (TCI, 40% in methanol) for 5 sec which is followed by another step of HI vapor for 30 seconds. The films were annealed at 100 $^{\circ}$ C for 1 hour. Then, the PCBM solution (dissolved in ortho-dichlorobenzene with a concentration of 20 mg/mL) was spin coated on top of the perovskite layer at 1500 rpm for 35 s. The substrate was annealed at 100 $^{\circ}$ C for 10 min. The device was finished by evaporating Al (60 nm) in a base pressure of 2×10^{-6} mbar. The device area was defined through a shadow mask from the overlap of the ITO and aluminum electrodes (10.9 mm²).

Device Characterization. The current density-voltage (J-V) measurement of the devices was conducted on a computer controlled Keithley 2602A source meter. The J-V measurement system uses a solar simulator with a Class-A match to the AM1.5 Global Reference Spectrum. Film absorption spectra of the films were compared with a Shimadzu UV-2600 UV-Vis spectrophotometer. Atomic force microscopy (AFM) images of the samples were recorded on a ParkSystems XE-100E microscope. X-ray diffraction (XRD) measurements were performed

with a Bruker D8 Discover X-ray diffractometer with copper K- α target X-ray tube. Film thickness measurements were determined with Ambios XP-200.

Photovoltaic Performance. The device architecture used in this study is given in Figure 2. The best device gave a PCE of 9.6% with an open circuit voltage (V_{oc}) of 0.77 V, a short-circuit density of (J_{sc}) of 38.1 mA/cm², and FF of 0.33 as shown in Figure 3. Considering the extremely high short circuit current density and the small fill factor of 0.33, PCE of 9.6% can easily be improved via further optimization.

Optical Spectroscopy. Optical absorbance of the film is given in Figure 4. The extrapolated onset absorption of perovskite films gives a band gap of 1.57 eV, in agreement with the literature reports [Xiao, Z. et al., Efficient, high yield perovskite photovoltaic devices grown by interdiffusion of solution-processed precursor stacking layers. *Energy Environ. Sci.* **2014**, 7, 2619]. The relatively high intensity of the peaks at ca. 750 nm and ca. 500 nm indicates good formation of perovskite crystals.

Surface morphology. AFM studies were performed to evaluate the quality of the film. The surface roughness (R_q) of the film is mainly limited by the predeposited PbI₂ film. The R_q value of the PbI₂ film is 6.5 nm whereas R_q value of the CH₃NH₃PbI₃ film is 8.5 nm. The grain sizes are also comparable as shown in Figure 5. The typical thickness of perovskite films has been measured as 290 nm, slightly smaller than the optimum thickness of 300 nm [Momblona, C. et al., Efficient methylammonium lead iodide perovskite solar cells with active layers from 300 nm to 900 nm. *Appl. Mat.* **2014**, 2, 081504].

XRD measurements. We further investigated the effect of vapor deposition on crystallization with XRD technique. The major diffraction peak of PbI₂ film was found at 12.8° as shown in Figure 6. CH₃NH₃PbI₃ film possess peaks that can be attributed to either CH₃NH₃PbI₃ or PbI₂ crystals. The diffraction peaks of CH₃NH₃PbI₃ crystal at 14.3°, 28.6°, and 43.3° can be assigned to (110), (220), and (330) planes, respectively. The comparison of (110) plane peak of CH₃NH₃PbI₃ crystal with respect to strong diffraction plane peak of PbI₂ crystal can be used to evaluate the extent of perovskite film formation. In this regard, it can be said that there is a good level of conversion of PbI₂ crystals to the CH₃NH₃PbI₃ crystal. The presence of PbI₂ crystal diffraction peaks indicate the perovskite formation is not complete and may explain the relatively poor fill factors of the devices obtained from these films compared to state of

art. The device performances can be optimized by increasing the conversion of PbI_2 crystal to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal.

Conclusions

In conclusion, we present a sequential vapor deposition method for the fabrication of perovskite solar cells. The method provides a means to achieve smooth perovskite thin film surfaces with minimal pin holes or cracks. Solar cells fabricated by employing the said perovskite regions exhibit excellent short circuit current densities and potential for superior power conversion efficiency with high reproducibility. The short circuit current density surpassing 38 mA/cm^2 is a new record for solution-processed photovoltaics and organic or hybrid inorganic/organic solar cells in general. Our findings enable completely new routes for the fabrication of perovskite-based photovoltaic devices as any preformed metal halide structure may be converted into the desired perovskite by this simple vapor deposition technique. Solar cells that are fabricated using this procedure exhibit not only excellent performance but also show very promising scalability for large area applications.

CLAIMS

1. A method for producing a nanocrystalline organic-inorganic perovskite layer, the method comprising the steps of:
 - a) applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts; and
 - b) applying and/or depositing one or more acids in vapor form; and
 - c) applying and/or depositing one or more amines/amine derivatives in vapor form; and
 - d) annealing the existing filmwherein steps a), b), c), and d) may be conducted in any order, either sequentially or simultaneously.
2. A method for producing a photoactive region which comprises:
 - (i) providing a first region;
 - (ii) disposing a second region on the first region, which second region comprises a layer of a perovskite semiconductor produced by the method comprising the steps a), b), c), and d) of the previous claim
 - (iii) disposing a third region on the second region, wherein:
 - the first region is an n-type region comprising at least one n-type layer and the third region is a p-type region comprising at least one p-type layer; or
 - the first region is a p-type region comprising at least one p-type layer and the third region is an n-type region comprising at least one n-type layer.
3. A method for producing an optoelectronic device, in which a photoactive region is sandwiched between two electrodes, and said method comprising:
 - (1) transparent carrier substrate with transparent electrode
 - (2) a first region with n/p-type layer;
 - (3) disposing a second region on the first region, which second region comprises the steps of claim 1:
 - a) applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts; and
 - b) applying and/or depositing one or more acids in vapor form; and

- c) applying and/or depositing one or more amines/amine derivatives in vapor form; and
- d) annealing the existing film

wherein steps a), b), c), and d) may be conducted in any order, either sequentially or simultaneously.

- (4) disposing a third region with p/n-type layer on the second region,
- (5) deposition of a counter electrode.

4. A method for producing any optoelectronic device that operates in tandem with the optoelectronic device in the previous claim.

5. The method of any one of the preceding claims, wherein said film comprising said perovskite layer is formed on the first region by the following steps:

- 1) performing step a), i.e., applying and/or depositing a film comprising and/or consisting essentially of one or more divalent or trivalent metal salts
- 2) performing step b), i.e., applying and/or depositing one or more acids in vapor form
- 3) performing step c), i.e., applying and/or depositing one or more amines/amine derivatives in vapor form
- 4) performing another step b), i.e., applying and/or depositing one or more acids in vapor form
- 5) performing step d), i.e., annealing the existing film

6. The method of any one of the preceding claims, wherein said film comprising said one or more divalent or trivalent metal salts is applied and/or deposited by any one or more methods selected from: deposition from solution, deposition from a dispersion (for example, from a colloidal dispersion), deposition by thermal evaporation or sputtering, electrodeposition, atomic-layer-deposition (ALD), and formation of said metal salt in-situ. wherein;

Examples of deposition from solution encompass, for example, drop casting, spin-coating, dip-coating, curtain coating, spray-coating, doctor blading, screen printing and ink-jet printing.

7. The method of any one of the preceding claims, wherein said film comprising said one or more divalent or trivalent metal salts is applied and/or deposited by spin-coating a solution of said one or more divalent or trivalent metal salt at 2000 rpm or more, preferably 3000 rpm or more.

8. The method of claim 7, wherein the concentration said one or more divalent or trivalent metal salt in the spin-coating solution is 250 mg/mL or more.
9. The method of claim 5, wherein the carrier substrate is annealed between 50 °C and 140 °C, more preferably at 70 °C after step a) and the duration of annealing is between 0 to 1 hours, preferably between 5 minutes to 30 minutes.
10. The method of any one of the preceding claims, wherein vapors of acids and amines/amine derivatives in steps b) and c) can be obtained in (i) direct form; or (ii) from solutions under reduced pressure; or (iii) by heating the said chemicals in a controlled atmosphere.
11. The method of claim 10, wherein vapors of acids in step b) are obtained from concentrated or dilute acid solutions; and the vapors of amines/amine derivatives in step c) are obtained from concentrated or dilute amine/amine derivative solutions.
12. The method of any one of the preceding claims, wherein said film comprising one or more divalent or trivalent metal salts is exposed to one or more acid vapors and one or more amines/amine derivative vapors either directly or with a carrier gas in steps b) and c), respectively.
13. The method of any one of the preceding claims, wherein said film comprising one or more divalent or trivalent metal salts is exposed to one or more acid vapors and one or more amines/amine derivative vapors in a closed chamber where the partial pressures and the flow rates for the acid vapors, the amine/amine derivative vapors, and the corresponding carrier gases (if any) are fixed.
14. The method of claim 5, wherein the duration of step b) is anywhere between 0 seconds to 10 minutes, more preferably between 5 seconds to 2 minutes and the duration of step c) is anywhere between 0 seconds to 10 minutes, more preferably between 0 seconds to 30 seconds.

15. The method of claim 5, wherein the carrier substrate with the perovskite film is annealed between 60 °C and 180 °C, preferably between 90 °C and 120 °C, and more preferably at 100 °C in step d), and the duration of annealing is between 0 and 4 hours, preferably between 30 minutes to 2 hours.

16. The method of any one of the preceding claims, wherein said one or more divalent or trivalent metals salts, respectively, have the formula MX_2 and NX_3 ; wherein M is a divalent metal cation selected from the group consisting of Cu^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Cr^{2+} , Pd^{2+} , Cd^{2+} , Ge^{2+} , Sn^{2+} , Pb^{2+} , Eu^{2+} , or Yb^{2+} ;

N is a trivalent metal cation selected from the group of Bi^{3+} and Sb^{3+} ;

and X is independently selected from F^- , Cl^- , Br^- , I^- , NCS^- , CN^- , CH_3COO^- , and NCO^- ;

wherein said one or more acid is being independently selected from HX and said one or more amines/amine derivatives is being independently selected from primary, secondary, tertiary or quaternary organic ammonium compounds, including N-containing heterorings and ring systems, preferably in the form of R^1NH_2 , R^1R^2NH , $R^1R^2R^3N$, $R^1(NH_2)_2$ where R^1 , R^2 and R^3 having from 1 to 60 carbons and 1 to 20 heteroatoms.

17. The method of any one of the preceding claims, wherein said divalent or trivalent metal salt is PbI_2 or SnI_2 .

18. The method of any one of the preceding claims, wherein said acid is hydrogen iodide (HI).

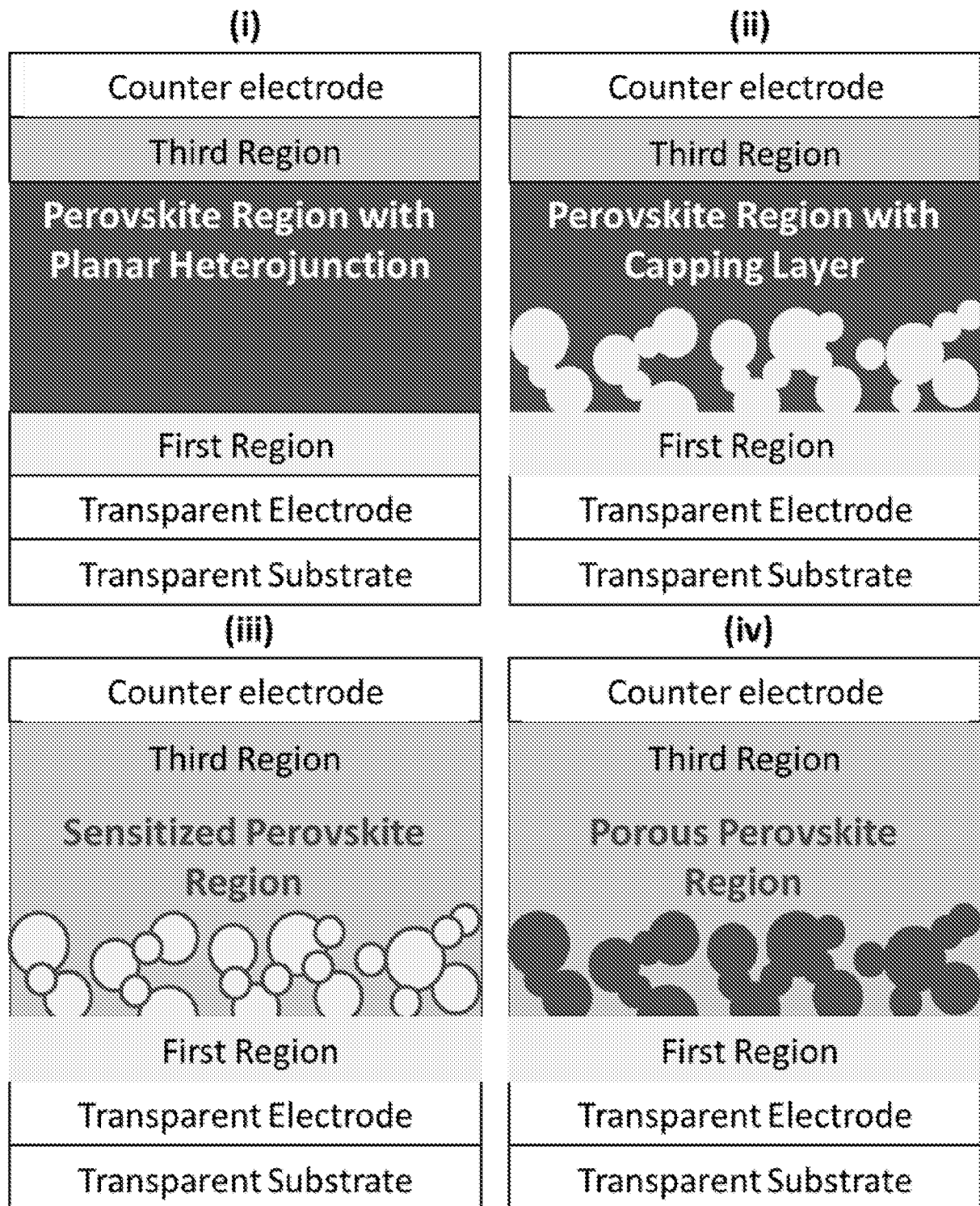
19. The method of any one of the preceding claims, wherein said amine/amine derivative is methylamine (CH_3NH_2) or formamidine (CH_4N_2).

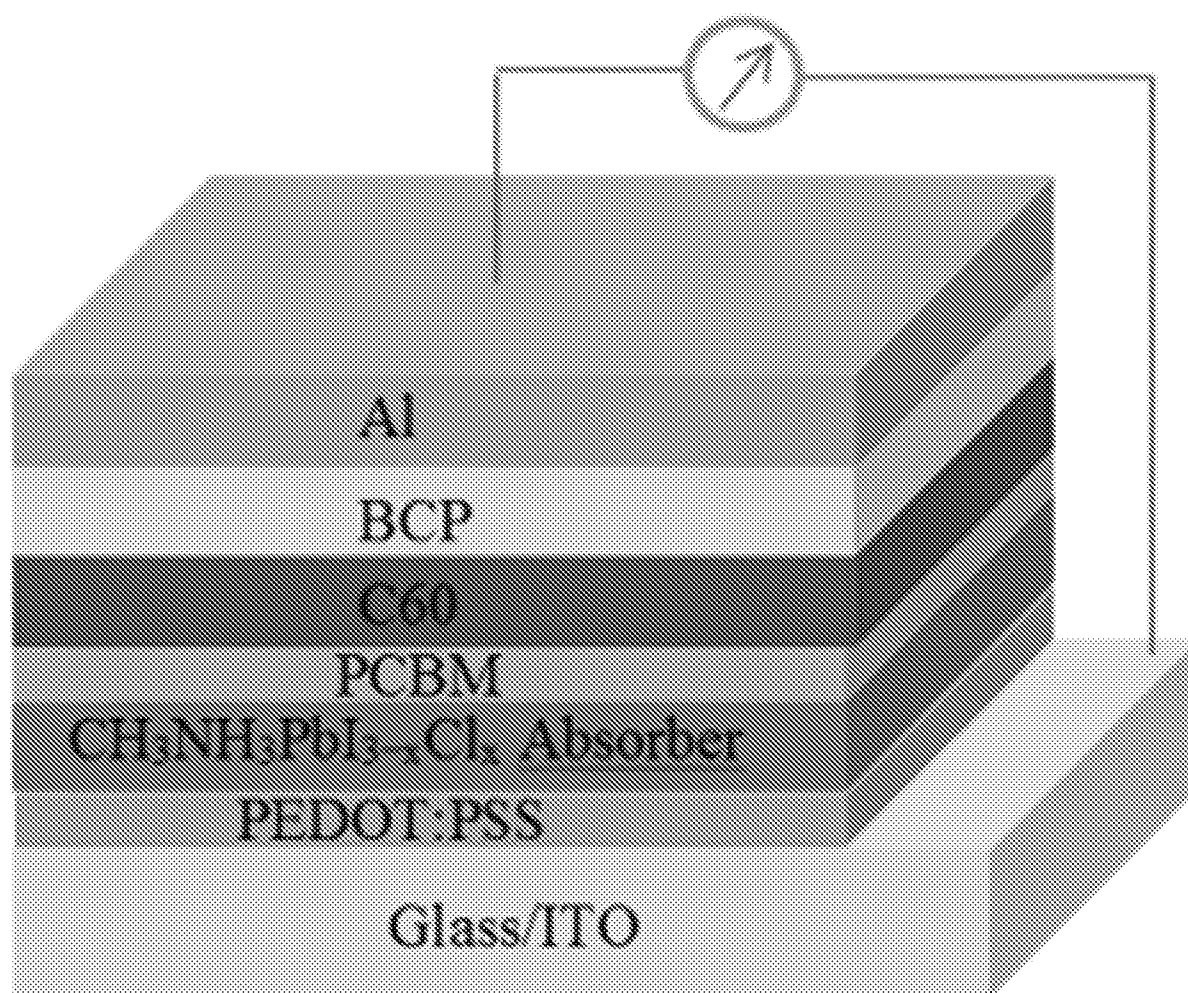
20. The method of claim 11, wherein HI vapor is applied from a concentrated or dilute HI solution, preferably from a concentrated solution with a concentration ranging from 48% to 67% in water by mass.

21. The method of claim 11, wherein methylamine vapor is applied from a concentrated or dilute amine solution, preferably from a concentrated solution with a weight percent larger than 40% in water or methanol.

22. The method of claim 10, wherein formamidine is directly applied in vapor form.

23. The perovskite layer obtainable by any one of the previous claims.
24. The optoelectronic device obtainable by any one of the previous claims.
25. A solar cell comprising organic-inorganic perovskite layer, wherein said solar cell exhibits a power conversion efficiency (PCE) of more than 9%, preferably more than 9.5% when exposed to AM1.5G light.
26. A solar cell comprising organic-inorganic perovskite layer, wherein said solar cell exhibits a short circuit current density of more than 20 mA/cm², preferably more than 30 mA/cm², more preferably more than 38 mA/cm² when exposed to AM1.5G light.

**FIG. 1**

**FIG. 2**

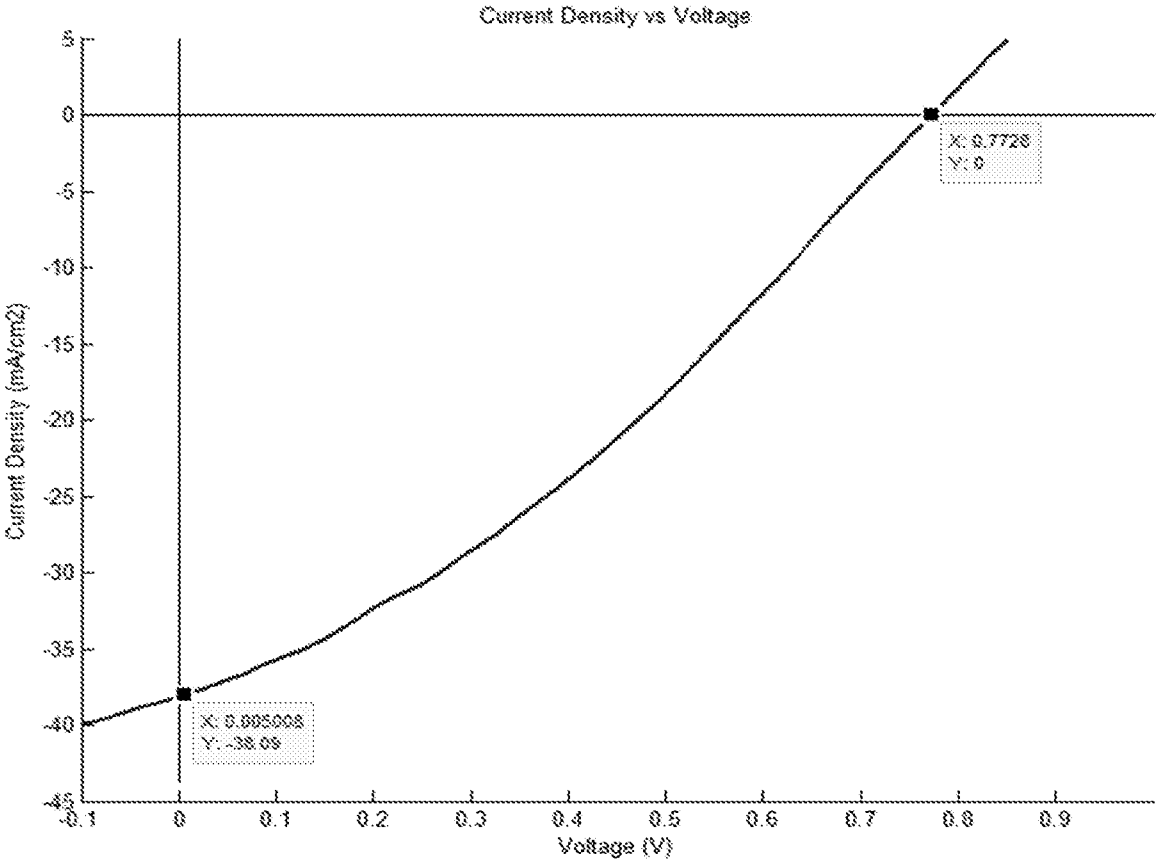
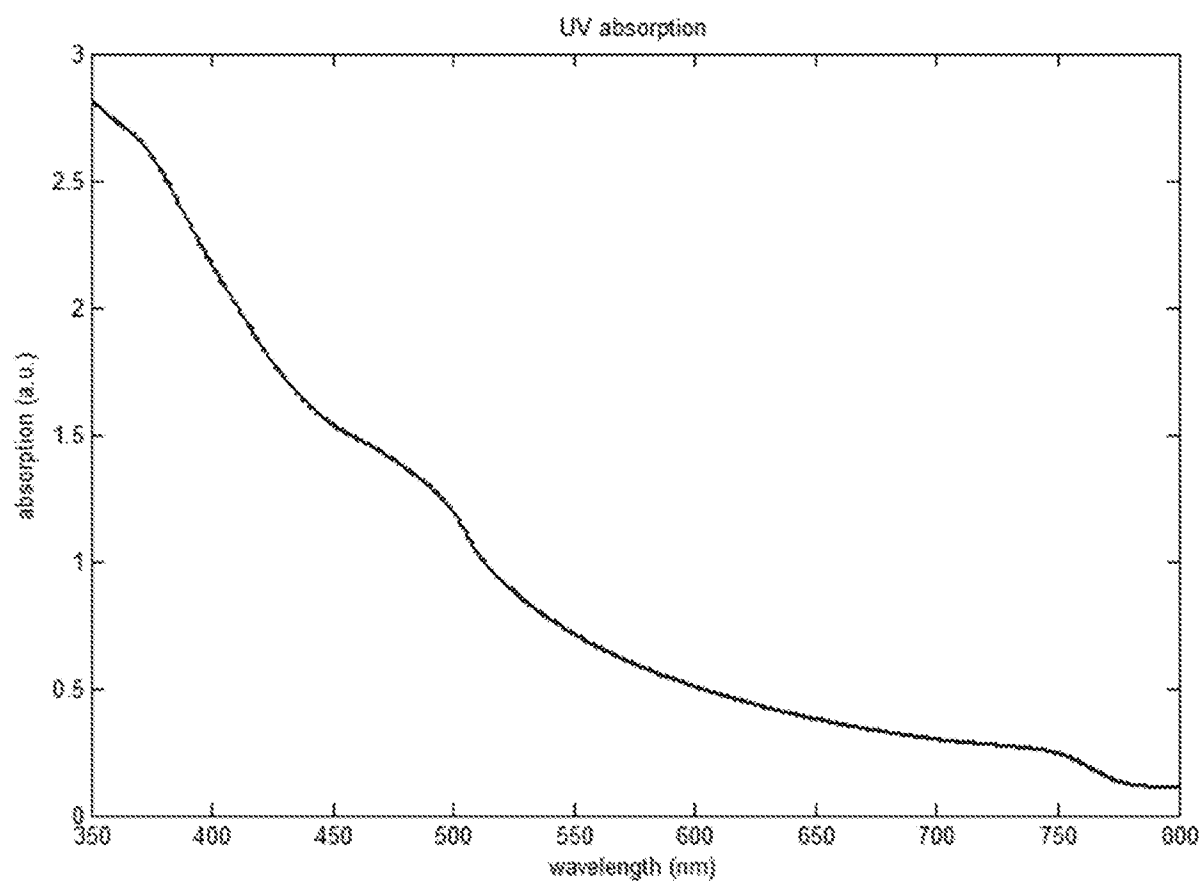


FIG. 3

**FIG. 4**

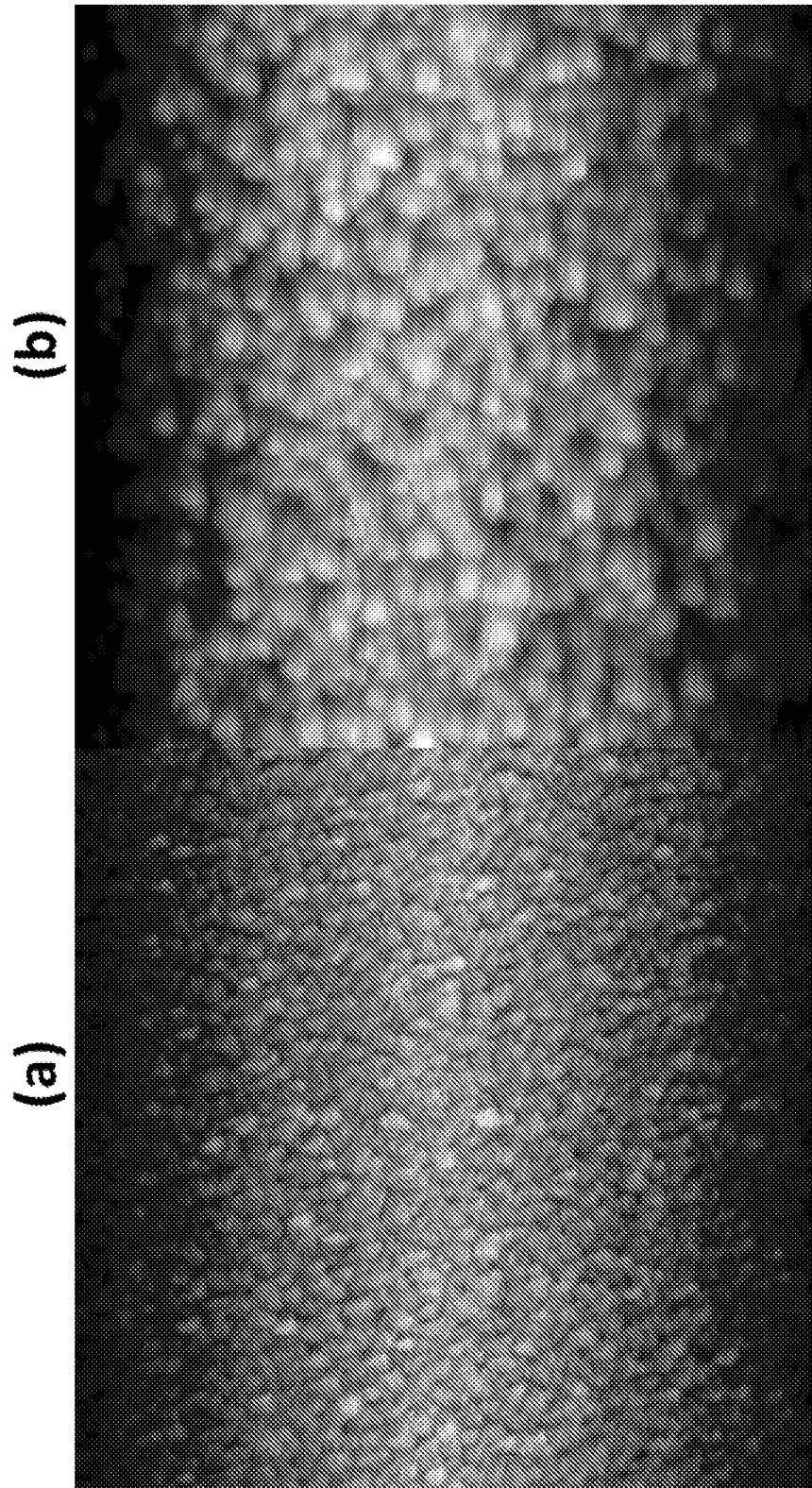
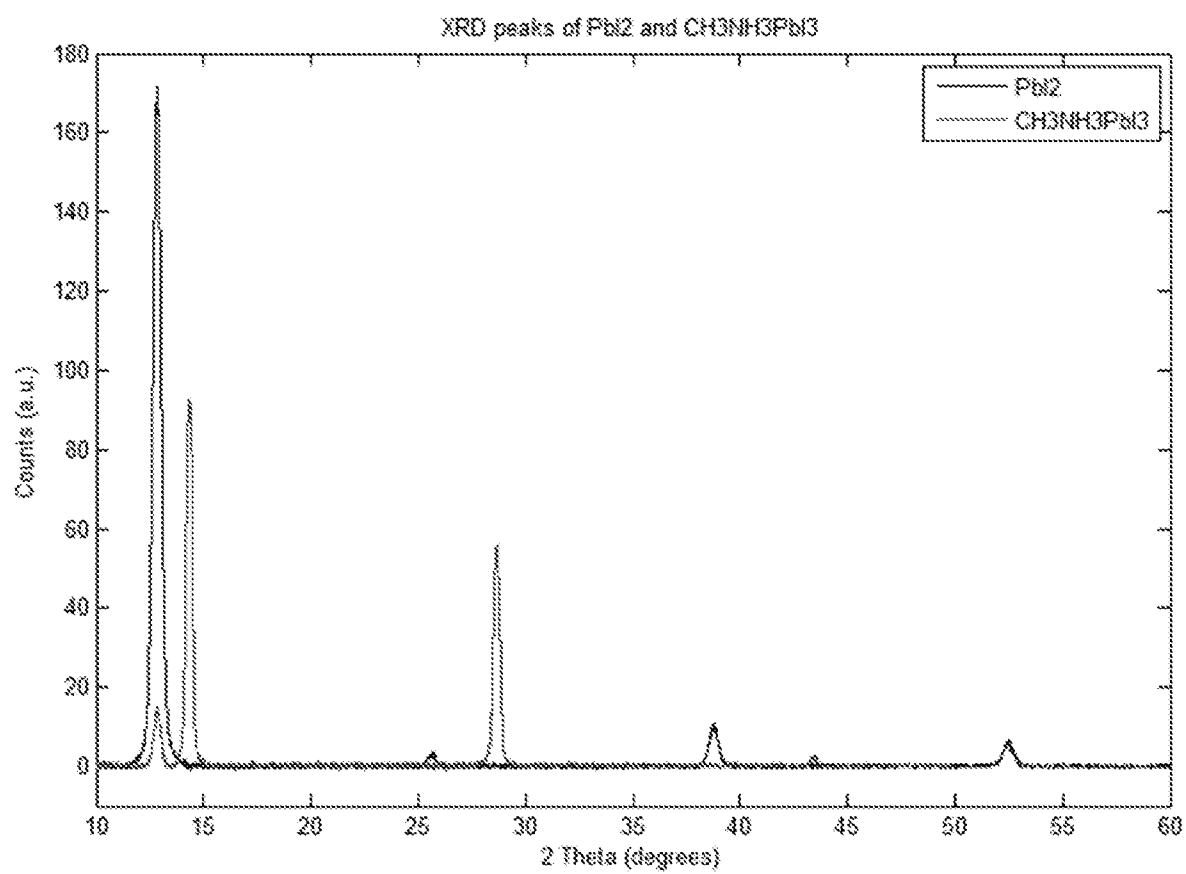


FIG. 5

**FIG. 6**

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/055290

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L51/00 C23C26/00
ADD.

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)
C23C H01L

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)

EPO-Internal, WPI Data, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 104 409 639 A (UNIV EAST CHINA NORMAL) 11 March 2015 (2015-03-11) abstract; paragraphs [0033], [0038], [0039], [0045]; figure 2	1-22
A	----- EP 2 846 371 A1 (ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE EPFL [CH]; UNIV VALENCIA [ES]) 11 March 2015 (2015-03-11) paragraph [0094]; figure 2A ----- -/-	1-26

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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

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

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"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

2 December 2015

Date of mailing of the international search report

09/12/2015

Name and mailing address of the ISA/

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Authorized officer

Peijzel, Paul

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/055290

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WEI E. I. SHA ET AL: "The efficiency limit of CH ₃ NH ₃ PbI ₃ perovskite solar cells", APPLIED PHYSICS LETTERS, vol. 106, no. 22, 1 June 2015 (2015-06-01) , page 221104, XP055232586, 2 Huntington Quadrangle, Melville, NY 11747 ISSN: 0003-6951, DOI: 10.1063/1.4922150	23-26
A	page 3; table 1	1-22
X	----- MINGZHEN LIU ET AL: "Efficient planar heterojunction perovskite solar cells by vapour deposition", NATURE, vol. 501, no. 7467, 11 September 2013 (2013-09-11), pages 395-398, XP055097500, ISSN: 0028-0836, DOI: 10.1038/nature12509	23-26
A	page 3; figures 1C, 3; table 1	1-22
X	----- NAM-GYU PARK: "Perovskite solar cells: an emerging photovoltaic technology", MATERIALS TODAY, vol. 18, no. 2, 1 March 2015 (2015-03-01), pages 65-72, XP055200828, ISSN: 1369-7021, DOI: 10.1016/j.matod.2014.07.007	23-25
A	figures 11,12	1-22
X	----- WANG QIONG ET AL: "Control of organic-inorganic halide perovskites in solid-state solar cells: a perspective", SCIENCE BULLETIN, SCIENCE CHINA PRESS, HEIDELBERG, vol. 60, no. 4, 4 February 2015 (2015-02-04), pages 405-418, XP035448479, ISSN: 2095-9273, DOI: 10.1007/S11434-015-0734-Y [retrieved on 2015-02-04]	23-25
A	Section 2.1; figures 2,5	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2015/055290

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 104409639	A	11-03-2015	NONE	

EP 2846371	A1	11-03-2015	EP 2846371 A1	11-03-2015
			WO 2015036905 A1	19-03-2015
