CLAIMS

1. A tandem photovoltaic device, comprising, in this superimposition order:

A/ a silicon-based sub-cell A comprising at least:

- a substrate made of crystalline, for example monocrystalline or polycrystalline, silicon in particular N-type or P-type doped; and

- at least one layer, distinct from said substrate, made of N- or P-doped amorphous or polycrystalline silicon;

and B/ a perovskite-based sub-cell B, comprising at least:

- a conductive or semiconductor layer, called lower layer, of the N type in the case of a NIP structure, or of the P type in the case of a PIN structure, and

- a composite layer, superimposed over said lower conductive or semiconductor layer, comprising at least one perovskite material and at least one material of the P type in the case of a NIP structure or of the N type material in the case of a PIN structure, and having a gradient of the perovskite material/P material mass ratio in the case of a NIP structure or perovskite material/N material mass ratio in the case of a PIN structure, decreasing in the direction from the interface between said composite layer and said lower conductive or semiconductor layer towards the opposite face of said composite layer,

the perovskite-based sub-cell B having a planar structure.

2. The tandem photovoltaic device according to the preceding claim, wherein said sub-cell A is a silicon heterojunction sub-cell or a TOPCon-type architecture sub-cell.

3. The tandem photovoltaic device according to claim 1 or 2, wherein said sub-cell A is a silicon heterojunction sub-cell, in particular comprises, in this stacking order:

- a first electrode $E1^A$;

- a layer made of N-doped or P-doped amorphous silicon;

- advantageously, a layer based on intrinsic amorphous silicon, serving as a passivation layer;

- said substrate made of crystalline, in particular monocrystalline, silicon in particular N-type doped;

- advantageously, a layer based on intrinsic amorphous silicon, serving as a passivation layer;

- a layer made of P-doped or N-doped amorphous silicon; and

- optionally, a second electrode E2A.

4. The tandem photovoltaic device according to claim 1 or 2, wherein said sub-cell A is a TOPCon-type architecture sub-cell, comprising in particular:

- said substrate made of N- or P-doped crystalline silicon;

~~5.~~ - at the face of the substrate intended to form the rear face of the tandem photovoltaic device, a layer made of highly N^+ or P^+ doped polycrystalline silicon, said layer made of highly doped polycrystalline silicon being separated from said substrate by a passivation layer made of oxide so-called “tunnel oxide”, in particular silicon oxide SiO_x, in particular SiO_2, or aluminium oxide AlO_x;

~~6.~~ - on the side of the opposite face of the substrate, at least one layer made of highly P+ or N+ doped crystalline or polycrystalline silicon of the electrical type opposite to that of the substrate.

5. ~~7.~~The tandem photovoltaic device according to any one of the preceding claims, wherein said perovskite-based sub-cell B comprises, in this stacking order:

- optionally a first electrode $E1^B$;

- said lower conductive or semiconductor layer of the N type in the case of a NIP structure or of the P type in the case of a PIN structure;

- said composite layer comprising at least one perovskite material and at least one material of the P type in the case of a NIP structure or of the N type in the case of a PIN structure, and having a gradient of the perovskite material/P material mass ratio in the case of a NIP structure or perovskite material/N material mass ratio in the case of a PIN structure, decreasing in the direction from the interface between said composite layer and said lower conductive or semiconductor layer towards the opposite face of said composite layer; and

- a second electrode, called the upper electrode, $E2^B$, in particular formed of a layer made of metallised transparent conductive oxide.

6.~~8.~~ The tandem photovoltaic device according to any one of the preceding claims, wherein said perovskite material and said P-type or N-type material form within the composite layer of said perovskite-based sub-cell B, over a thickness of at least 10 nm, in particular over a thickness comprised between 10 nm and 150 nm, an interpenetrating structure, said interpenetrating structure being more particularly composed of said P-type or N-type material(s) incorporated into a crystallised perovskite matrix.

7.~~9.~~ The tandem photovoltaic device according to any one of the preceding claims, wherein said composite layer of said perovskite-based sub-cell B has, in the direction from the interface between said composite layer and said underlying conductive or semiconductor layer towards the face of said composite layer, opposite to the interface between the composite layer and the underlying conductive or semiconductor layer:

- a first area primarily formed of the perovskite-type material, or exclusively made up of the perovskite-type material;

- an area comprising a mixture of the perovskite and P-type materials in the case of a NIP structure or N-type materials in the case of a PIN structure; and

- an area formed primarily, and possibly consisting exclusively of the P-type material in the case of a NIP structure or of the N type material in the case of a PIN structure.

8.~~10.~~ The tandem photovoltaic device according to any one of the preceding claims, wherein the interface between the composite layer and the underlying conductive or semiconductor layer at the sub-cell B forms a planar junction.

9.~~11.~~ The tandem photovoltaic device according to any one of the preceding claims, wherein said composite layer has a thickness smaller than or equal to 1 µm, in particular comprised between 200 and 800 nm and more particularly comprised between 300 and 600 nm.

10.~~12.~~ The tandem photovoltaic device according to any one of the preceding claims, wherein the perovskite material of said composite layer is of formula ABX_3, with:

~~13.~~ A representing a cation or a combination of metallic or organic cations;

~~.~~ B representing one or more metallic element(s), such as lead, tin, bismuth and antimony; and

~~.~~ X representing one or more anion(s), in particular one or more halide(s), and more particularly selected from among chloride, bromide, iodide and mixtures thereof,

said perovskite material being in particular of formula $Cs_xFA_{1-x}Pb(I_{1-y}Br_y)_3$ with $x<0.17$; $0<y<1$ and FA symbolising the formamidinium cation.

11.~~14.~~ The tandem photovoltaic device according to any one of the preceding claims, wherein said sub-cell B is:

- of the NIP structure, wherein the P-type material of said composite layer is selected from among π-conjugated conductive or semiconducting polymers, possibly doped; in particular said P-type material is selected from among a mixture of PEDOT and PSS, and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), possibly doped with a lithium

salt such as lithium bis(trifluoromethane)sulphonide (LiTFSI) and/or 4-tert-butylpyridine; or

- of the PIN structure, wherein the N-type material of said composite layer is selected from among N-type metal oxides, in particular selected from among zinc oxide, titanium oxides TiO_x with x comprised between 1 and 2, tin oxide, doped zinc oxides, for example aluminium-doped zinc oxide, indium-doped zinc oxide, gallium-doped zinc oxide, doped titanium oxides, for example titanium oxide doped with nitrogen, phosphorus, iron, tungsten or manganese, tin oxides doped for example with fluorine, and mixtures thereof; and more particularly from among tin oxide, doped zinc oxides, in particular aluminium-doped zinc oxide and mixtures thereof.

12.~~15.~~ The tandem photovoltaic device according to any one of claims 3 and ~~4~~5 to 9~~11~~, said device being of the HET/perovskite type with a 2T structure, comprising, in this superimposition order, at least:

- a sub-cell A as described according to claim 3, comprising in this superimposition order:

. said first electrode denoted $E1^A$, in particular formed of a metallised conductive transparent layer;

. said layer made of N-doped or P-doped amorphous silicon, preferably made of N-doped or P-doped hydrogenated amorphous silicon;

. advantageously, said layer based on intrinsic amorphous silicon, preferably hydrogenated, serving as a passivation layer;

. said substrate made of crystalline, in particular monocrystalline and in particular N-type doped, silicon;

. advantageously, said layer based on intrinsic amorphous silicon, preferably hydrogenated, serving as a passivation layer;

. said layer made of P-doped or N-doped amorphous silicon, preferably P-doped or N-doped hydrogenated amorphous silicon;

- an electronically conductive or semiconductor intermediate layer, called “recombination layer”;

- a sub-cell B as described according to any one of claims 45 to 911, comprising in this superimposition order:

. said N-type or P-type conductive or semiconductor layer, and

. said perovskite/P material or N material composite layer;

. said second electrode, called the upper electrode, $E2^B$, in particular formed of a metallised transparent conductive oxide layer.

13.16. A method of manufacturing a tandem photovoltaic device according to any one of claims 1 to 1012, comprising at least the following steps:

(a) making said silicon-based sub-cell A; and

(b) making said perovskite-based sub-cell B, in which said composite layer is formed at the surface of said N-type or P-type lower conductive or semiconductor layer, through at least the following steps:

(i) forming, on the surface of said lower conductive or semiconductor layer, a wet film from a solution of precursors of the perovskite material in one or more solvent(s), said solvent(s) being selected in particular from among dimethylformamide, dimethyl sulfoxide, gamma-butyrolactone and mixtures thereof;

(ii) adding to said wet film of step (i) at least one material of the P type in the case of the formation of a NIP stack, or of the N type in the case of a PIN stack; and

(iii) subjecting the whole to a heat treatment conducive to the elimination of the solvents and the crystallisation of the perovskite material.

14.17. The method according to the preceding claim, wherein step (ii) is carried out by depositing, at the surface of said wet film of step (i), a formulation of at least said P-type material in the case of the formation of a NIP stack or N-type material in the case of the formation of a PIN stack, in one or more solvent(s), called “anti-solvents”, in which the perovskite precursors are not soluble, said anti-solvent(s) being more particularly selected from among diethyl ether; dichloromethane; aromatic compounds with one, two or three substituted ring(s), in particular substituted by one or more alkyl, in particular methyl, group(s) and/or halogen(s), in particular chlorine, such as

toluene, chlorobenzene, xylene, methylnaphthalene; and mixtures thereof; preferably the anti-solvent being toluene.

15.~~18.~~ The method according to claim 10~~13~~ or 11~~14~~, wherein steps (i) and (ii) are carried out consecutively by spin-coating, preferably step (ii) being carried out without stopping the rotation of the rotating platform of the spin coater.

16.~~19.~~ The method according to any one of claims 10~~13~~ to 12~~15~~, wherein step (iii) is carried out by thermal annealing at a temperature comprised between 60 and 150°C, in particular between 80 and 120°C, in particular for a duration comprised between 5 and 120 minutes, in particular between 15 and 90 minutes and more particularly between 30 and 60 minutes.