

EPITAXIAL GROWTH OF $\text{Sb}_2(\text{S,Se})_3$ THIN FILM ON SnO_2/CdS SUBSTRATE BY SOLUTION METHOD

Field of Invention

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The current invention relates to the growing of $\text{Sb}_2(\text{S,Se})_3$ film on a substrate by solution method, and a light absorbing device obtained through the use of said method.

Background

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15 Antimony chalcogenides including Sb_2S_3 , Sb_2Se_3 and mixed-anion $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ ($0 \leq x \leq 1$) alloy have gained great interest for solar cell applications due to their superior optoelectronic properties, which enable an impressive progress in recent years delivering record power conversion efficiency (PCE) of 7.5%, 9.2% and 10%, respectively (Y. C. Choi *et al.*, *Adv. Funct. Mater.* **2014**, 24, 3587-3592; Z. Li *et al.*, *Nat. Commun.* **2019**, 10, 125; and R. Tang *et al.*, *Nat. Energy* **2020**, 5, 587-595). In particular, $\text{Sb}_2(\text{S,Se})_3$ possesses a high absorption coefficient ($>10^5 \text{ cm}^{-1}$) in visible region and tunable band gap between 1.1–1.8 eV. The non-toxicity and earth-abundance of its constituents make $\text{Sb}_2(\text{S,Se})_3$ a promising candidate to compete with existing materials for commercial photovoltaics. Moreover, $\text{Sb}_2(\text{S,Se})_3$ has a stable single orthorhombic phase with a quasi-1D crystal structure (FIG. 1, Y. Zhou *et al.*, *Nat. Photonics* **2015**, 9, 409-415; and X. Wen *et al.*, *Nat. Commun.* **2018**, 9, 2179), resulting in anisotropic electrical properties in thin film (L. Guo *et al.*, *APL Mater.* **2019**, 7, 041105). It has been reported that conductivity along the $(\text{Sb}_4\text{X}_6)_n$ ($\text{X} = \text{S}$ or Se) ribbons (c-axis) is much higher than the other directions that require electron hopping between adjacent ribbons (T. Fujita *et al.*, *J. Phys. Soc. Jpn.* **1987**, 56, 3734-3739; and P. Bohac & P. Kaufmann, *Mater. Res. Bull.* **1975**, 10, 613-622). Therefore, high efficiency solar cells intrinsically require the vertical growth of $(\text{Sb}_4\text{X}_6)_n$ ribbons in the $\text{Sb}_2(\text{S,Se})_3$ absorber layer which is featured with dominant (hk1) planes, ensuring an efficient charge transport.

35 Theoretical calculations suggest that the (hk0) planes in $\text{Sb}_2(\text{S,Se})_3$ have lower surface energy than (hk1) planes (Y. Zhou *et al.*, *Nat. Photonics* **2015**, 9, 409-415). Hence, following minimum energy principle, the most-abundant surface of $\text{Sb}_2(\text{S,Se})_3$ will thus be (hk0), leading to the horizontal growth of $(\text{Sb}_4\text{X}_6)_n$ ribbons. Given this perspective, most attempts to modify the

crystal growth behavior of $\text{Sb}_2(\text{S,Se})_3$ have been performed under a well-controlled thermodynamic environment in conjunction with substrate selection. Wang *et al.* demonstrated a reduction in interface defects in a 5.93% efficiency device that employed randomly oriented ZnO substrate to induce the formation of [221]-oriented Sb_2Se_3 film by rapid thermal evaporation (RTE, L. Wang *et al.*, *Nat. Energy* **2017**, 2, 17046). By controlling the substrate temperature, Li *et al.* also obtained a preferentially [211]- and [221]-oriented Sb_2Se_3 film on TiO_2 substrate via RTE process, and a PCE of 7.62% was achieved for the device with a high short circuit current density (J_{SC}) of 29.9 mA/cm^2 (K. Li *et al.*, *Adv. Mater.* **2019**, 31, e1903914).

In order to fabricate vertically oriented $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$, some essential measures must be taken to control the initial nucleation and growth processes. For the growth of high-quality thin film or single crystal with desired orientation, epitaxial growth technique is widely considered to be the most powerful method so far. As shown in FIG. 2a, the term ‘Epitaxial’ refers to the elaborate growth of a target crystalline material on the well-defined surface of a selected crystalline substrate, with the overlayer having the same crystalline orientation as the substrate. This unique way of film growth enables epitaxial growth a high level of control over the composition, preferred orientation, exposed facets of target material, and the relative crystal orientation relationship to the substrate. It should be noted that conventionally, the epitaxial layer is generally grown on rigid single-crystalline substrates with a close lattice matching and strong chemical bonding formed at the interface. Recently, there has been considerable interest in growing epitaxial films through weak interface interactions such as van der Waals (vdW) interaction (herein mica was widely used as the substrate), which greatly extends the scope of application (FIG. 2b, H. Kum *et al.*, *Nat. Electron.* **2019**, 2, 439-450; and X. Wen *et al.*, *ACS Appl. Energy Mater.* **2020**, 3, 4589-4599). It should be noted that, for a specific film growth, epitaxial growth can be further divided into homo- and hetero-epitaxy, where the former refers to the growth on a same crystal surface of its own and the latter refers to the more general case, where film and substrate materials are different in composition and crystal structure, but have similar physical properties at the interface. Obviously, the realization of a specific functional film with preferred orientation and constructing heterojunction in-situ using epitaxial growth technique possesses overwhelming advantage in electrical and physical properties at the interface, mainly reflected in the facilitated charge transport by removing potential interfacial defects. With the development of science, more new technologies are being introduced to the fields of epitaxial growth. For vacuum-based epitaxial methods, molecular beam epitaxy (MBE), chemical-vapor deposition (MOCVD), vapor transport deposition (VTD), and atomic layer deposition (ALD) have already become the mainstream technologies. In addition, some non-vacuum solution-based epitaxy methods, such as colloidal synthesis and chemical reduction, have recently been developed for the

epitaxial fabrication of a wide range of heterojunctions on a large scale and in high yield (C. Tan *et al.*, *Nat. Rev. Mater.* **2018**, 3, 1-13). Nevertheless, the control of orientation in solution-processed films has proved to be more challenging, commonly leading to the horizontal growth of $(\text{Sb}_4\text{X}_6)_n$ ribbons.

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In general, most of the reported studies on epitaxial fabrication of functional layer focused on the vacuum-based techniques which show great capability in growing high quality epitaxial p-n interface for photovoltaics, but they are expensive and time-consuming, and thereby impractical for industrialized production. For the non-vacuum-based methods, the solar cell device is considered to be fabricated at relatively low cost. However, the underlying film growth mechanism for the current demonstration is based on van der Waals interaction, in which an epitaxial lift-off and layer transfer process is generally required to form a working heterojunction if applied to a real solar cell device (H. Kum *et al.*, *Nat. Electron.* **2019**, 2, 439-450). Such destructive process would inevitably induce potential interface defects, thus reducing the overall efficiency.

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Therefore, there exists a need of an epitaxial growth process that is in-situ, low cost and repeatable, to realize the vertical growth of $\text{Sb}_2(\text{S,Se})_3$ layer *in-situ* on a substrate.

20 Summary of Invention

Aspects and embodiments of the invention will now be discussed by reference to the following numbered clauses.

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1. A method of forming a film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$, comprising the steps of:

(a) placing a substrate, comprising:

a first layer formed from SnO_2 ; and

a second layer on top of the first layer, the second layer providing a surface for $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ growth, the second layer formed from CdS in hexagonal form, where the surface is substantially formed from a (100) facet of the hexagonal CdS,

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against a wall of a vessel, such that the substrate is positioned at an angle relative to a base of the vessel;

(b) immersing the substrate in an aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ and conducting a hydrothermal reaction for a period of time at a temperature of from 100 to 150 °C

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to grow the film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ on the second layer of the substrate, wherein the precursor solution further comprises a cadmium (II) salt in an amount to provide a molar percentage of Cd relative to the amount of Sb ($n_{\text{Cd}}/n_{\text{Sb}}$) of from 1 to 5%; and x is from 0 to 1.

2. The method according to Clause 1, wherein the product of step (b) of Clause 1 is annealed at a temperature of from 250 to 400 °C, such as from 300 to 350 °C, such as about 335 °C for a period of from 5 minutes to 1 hour, such as from 10 to 40 minutes, such as from 15 to 30 minutes, such as about 20 minutes.
3. The method according to Clause 1 or Clause 2, wherein:
 - (ai) the period of time in step (b) of Clause 1 is from 1 to 10 hours, such as from 2 to 4 hours, such as about 3.5 hours; and/or
 - (aii) the temperature in step (b) of Clause 1 is from 120 to 150 °C, such as from 125 to 130 °C.
4. The method according to any one of the preceding clauses, wherein the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ comprises $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 3\text{H}_2\text{O}$ and one or both of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and $\text{SeC}(\text{NH}_3)_2$, optionally wherein the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ comprises $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, but not $\text{SeC}(\text{NH}_3)_2$.
5. The method according to any one of the preceding clauses, wherein the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ comprises a molar ratio of Sb:S of from 1:2 to 1:5 (e.g. about 1:4.8) and a molar ratio of Sb:Se of from 1:0 to 1:0.3 (e.g. about 1:0.24).
6. The method according to any one of the preceding clauses, wherein the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ comprises a cadmium (II) salt in an amount ($n_{\text{Cd}}/n_{\text{Sb}}$) of from 1 to 4%, such as from 2 to 3.5%, such as from 2.5 to 3.25%, such as about 3%.
7. The method according to any one of the preceding clauses, wherein the angle is from 20 to 60°, such as about 40°.
8. The method according to any one of the preceding clauses, wherein the substrate is formed by the steps of:
 - (bi) providing a precursor substrate comprising a first layer of SnO_2 and a second layer formed from CdS ; and
 - (bii) coating a C_1 to C_3 alcohol solution of an oversaturated cadmium (II) salt for a first period of time on the precursor substrate to provide an intermediate substrate, which is then annealed for a second period of time at a temperature of from 350 to 500 °C, optionally wherein the C_1 to C_3 alcohol is methanol.
9. The method according to Clause 8, wherein:

- (ci) the second period of time is from 5 to 20 minutes, such as about 10 minutes; and/or
- (cii) the temperature is from 400-420 °C, such as 415 °C.

10. The method according to Clause 8 or Clause 9, wherein the precursor substrate is
5 formed by the steps of:

- (di) providing a SnO₂ substrate comprising a surface formed by SnO₂; and
- (dii) immersing the SnO₂ substrate in a CdS precursor solution at a temperature of from 45 to 100 °C for a period of time to form the precursor substrate, optionally wherein the SnO₂ substrate further comprises an electrode layer, more optionally wherein the electrode layer is
10 formed from ITO glass or, more particularly, FTO glass.

11. The method according to Clause 10, wherein:

- (ei) the period of time is from 10 to 20 minutes, such as about 15 minutes; and/or
- (eii) the temperature is from 60 to 80 °C, such as about 65 °C.

12. The method according to Clause 8 or Clause 9, wherein the SnO₂ substrate is formed
by the steps of:

- (fi) providing a blank substrate material having a surface; and
- (fii) spin-coating the surface of the blank substrate with a solution comprising SnO₂
nanoparticles to provide the SnO₂ substrate.

13. The method according to Clause 12, wherein:

- (gi) the SnO₂ nanoparticles have a diameter of from 1 to 20 nm, such as from 3 to 4 nm;
and/or

(gii) the SnO₂ substrate obtained in step (fii) of Clause 12 is subjected to annealing for a
period of time at an elevated temperature, optionally wherein the period of time is from
10 minutes to 1 hour, such as about 30 minutes, and the elevated temperature is from 100 to
200 °C, such as about 150 °C; and/or

(giii) the spin-coating in step (fii) of Clause 12 was conducted at a speed of from 1000 to
3500 rpm for a period of time, optionally wherein the speed is about 2500 rpm and/or the
period of time is about 30 seconds.

14. The method according to any one of the preceding clauses, wherein:

(aai) the hexagonal CdS has (100) and (101) facets and the surface of the second layer is
formed from the (100) and (101) facets of the hexagonal CdS, where the ratio of intensity of
the (100) facet to the (101) facet in the X-ray diffraction pattern is greater than or equal to 1.3;
and/or

(aaii) the cadmium (II) salt is CdSO_4 or has the formula CdX_2 , where each X is a halide or NO_3 , optionally wherein X is I, Br or, more particularly, Cl;

(aa iii) the relationship of the second layer and the film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ to each other is $(001)_d$ $[001]_d \parallel (100)_s$ $[210]_s$.

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15. The method according to any one of the preceding clauses, wherein a hole transport layer is placed on the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ and an electrode is placed on the hole transport layer, optionally wherein the hole transport layer is spiro-OMeTAD and the electrode is gold and/or silver (e.g. a layer of gold and/or silver that is from 30 to 100 nm thick, such as 60 nm thick).

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16. A light absorbing device comprising:

a first electron transport layer formed of SnO_2 ;

a CdS layer on the first electron transport layer as a second electron transport layer;

a $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer on the CdS layer as a light absorbing layer; and

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a hole transport layer on the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer, wherein

the CdS layer is formed from CdS in hexagonal form, where the surface is substantially formed from a (100) facet of the hexagonal CdS and the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer is formed from a plurality of parallel $(\text{Sb}_4\text{X}_6)_n$ ribbons that extend from the CdS layer in a [001] direction.

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17. The light absorbing device according to Clause 16, wherein the relationship of the CdS layer and the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer to each other is $(001)_d$ $[001]_d \parallel (100)_s$ $[210]_s$.

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18. The light absorbing device according to Clause 16 or Clause 17, wherein the first electron transport layer formed of SnO_2 has a first surface and a second surface, where the first surface is attached to a transparent electrode material and the second surface is attached to the CdS layer.

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19. The light absorbing device according to Clause 18, wherein the transparent electrode material is selected from ITO glass or, more particularly, FTO glass.

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20. The light absorbing device according to any one of Clauses 16 to 19, wherein the hexagonal CdS has (100) and (101) facets and the surface of the second layer is formed from the (100) and (101) facets of the hexagonal CdS, where the ratio of intensity of the (100) facet to the (101) facet in the X-ray diffraction pattern is greater than or equal to 1.3.

21. The light absorbing device according to any one of Clauses 16 to 20, wherein:

(hi) the hole transport layer has a first surface attached to the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer and a second surface attached to an electrode material; and/or

(hii) the hole transport layer is an organic semiconductor or an inorganic semiconductor with p-type conductivity, optionally wherein the hole transport layer is selected from one or more of the group consisting of P3HT, PbS, MnS, CuSCN, and, more particularly, spiro-OMeTAD.

22. The light absorbing device according to Clause 21, wherein the electrode material is a layer of gold and/or silver (e.g. a layer of gold and/or silver that is from 30 to 100 nm thick, such as 60 nm thick).

23. The light absorbing device according to any one of Clauses 16 to 22, wherein the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer is formed by a plurality of $(\text{Sb}_4\text{X}_6)_n$ ribbons oriented in (hk1) planes, optionally wherein the $(\text{Sb}_4\text{X}_6)_n$ ribbons display one or more (hk1) planes selected from the (101), (111), (211) and (221).

24. The light absorbing device according to Clause 23, wherein one or more of the following apply:

the (101) plane has a texture coefficient of greater than or equal to 1.80;

the (111) plane has a texture coefficient of greater than or equal to 1.20;

the (211) plane has a texture coefficient of greater than or equal to 1.10; and

the (221) plane has a texture coefficient of greater than or equal to 1.10.

25. The light absorbing device according to any one of Clauses 16 to 24, wherein the light absorbing device displays a power conversion efficiency of from 9.0 to 10%, such as about 9.24%.

Drawings

FIG. 1 depicts the crystal structure of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$, wherein the $(\text{Sb}_4\text{X}_6)_n$ ($\text{X} = \text{S}$ or Se) ribbons are covalently bonded through Sb-S(e) bonds along c-axis. The single ribbon consists of two trigonal SbX_3 and two square SbX_5 pyramids. The in-plane ribbons are held together in parallel along the b-axis via weak van der Waals force, forming layered sheets of $\text{Sb}_2(\text{S},\text{Se})_3$. In this structure, the conductivity along the ribbon is about two orders of magnitude higher than that perpendicular to it. In addition, the grain boundaries (GBs) parallel to c-axis are free of dangling bonds (Y. Zhou *et al.*, *Nat. Photonics* **2015**, 9, 409-415; R. Kondrotas, C. Chen & J. Tang, *Joule* **2018**, 2, 857-878; and T. Fujita *et al.*, *J. Phys. Soc. Jpn.* **1987**, 56, 3734-3739). It

should be noted that, according to the orthorhombic Pbnm structure, the dominant planes will be those (hk1) when the $(\text{Sb}_4\text{X}_6)_n$ ribbons grown vertically on the substrate with a small degree angle. In other words, (hk0) planes will dominate the film when the ribbons grown horizontally on the substrate.

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FIG. 2 depicts the illustration showing the (a) conventional epitaxial growth technique based on strong covalent bond, and (b) emerging epitaxial growth technique based on weak van der Waals (vdW) force.

10 **FIG. 3** depicts (a) schematic diagram of $\text{Sb}_2(\text{S,Se})_3$ device fabrication procedures; (b) contour map of $\text{Sb}_2(\text{S,Se})_3$ solar cell efficiency with different CdS growth time during chemical bath deposition (CBD) process and Cd concentration in hydrothermal system; and (c) texture coefficients of $\text{Sb}_2(\text{S,Se})_3$ fabricated with different Cd concentration.

15 **FIG. 4** depicts (a) the plot of CdS film thickness as the function of deposition time during the CBD process; and (b) the incident angle-dependent grazing incidence X-ray diffraction (GIXRD) analysis of CdS films. It can be seen that as the incident angle decreased from 0.8° to 0.4° , the main diffractions from (100) and (002) planes of hexagonal CdS almost maintained the same intensities, while the peak at 26.5° decreased significantly, in sync with the changing
20 of the diffractions coming from FTO substrate (labeled with *), indicating that the peak at 26.5° comes from the substrate rather than the CdS itself.

FIG. 5 depicts the detailed device parameters of $\text{Sb}_2(\text{S,Se})_3$ solar cells as the Cd concentration is increased from 0% to 4% (The deposition time of CdS substrates was the same, kept at 12
25 min during the CBD process).

FIG. 6 depicts the X-ray diffraction (XRD) patterns of $\text{Sb}_2(\text{S,Se})_3$ films prepared with increasing the Cd concentration from 0% to 4% during hydrothermal process.

30 **FIG. 7** depicts the Pawley fits of the powder XRD patterns of (a) hk0- $\text{Sb}_2(\text{S,Se})_3$ and (b) hk1- $\text{Sb}_2(\text{S,Se})_3$ thin film.

FIG. 8 depicts the Auger electron spectroscopy (AES) depth profile analysis of hk0- $\text{Sb}_2(\text{S,Se})_3$ and hk1- $\text{Sb}_2(\text{S,Se})_3$ films. The inset shows the schematic of corresponding signal shape (Cd)
35 coming from different films.

FIG. 9 depicts the plots of Gibbs free energy change as a function of temperature for reactions between Sb^{3+} and $\text{S}^{2-}/\text{Se}^{2-}$. It should be noted that the more negative ΔG is, the more favorable the reaction.

FIG. 10 depicts the X-ray photoelectron spectroscopy (XPS) analysis focusing on the bulk of $\text{hk0-Sb}_2(\text{S,Se})_3$ (top) and $\text{hk1-Sb}_2(\text{S,Se})_3$ (bottom) films. The core-levels of (a) S, (b) Se, (c) Sb, and (d) the calculated elements ratio of $(\text{S}+\text{Se})/\text{Sb}$ and $\text{Se}/(\text{S}+\text{Se})$ from XPS quantitative analysis. It should be noted that five positions have been checked in our study. Only one batch of spectra is presented here since other positions showed identical results.

FIG. 11 depicts (a) XRD pattern of CdS substrate after thermal treatment; (b) density functional theory (DFT) results showing the surface energies of (002), (101), (100) and (110) facets of hexagonal CdS. (The inset shows the corresponding crystal morphology calculated by Wulff construction method under the thermodynamic equilibrium state); the AFM image of CdS film (c) prepared by CBD method, and (d) after thermal treatment; and (e) after hydrothermal reaction (Samples were prepared by etching off the $\text{Sb}_2(\text{S,Se})_3$ layer with alkali solution).

FIG. 12 depicts (a) crystal structure showing two distinct atomic stacking orders on {100} and {101} facets of hexagonal CdS; and (b) schematic illustration (2D) showing the in-plane anchoring relationship between the (100) facet of hexagonal CdS and the end of $(\text{Sb}_4\text{X}_6)_n$ ribbon of $\text{Sb}_2(\text{S,Se})_3$.

FIG. 13 depicts the slab models of the bulk, (100), (002), (101) and (110) planes of hexagonal CdS used for obtaining surface energy by DFT calculation (R. Tran *et al.*, *Sci. Data* **2016**, 3, 160080).

FIG. 14 depicts (a) two distinct crystal growth characteristics of $\text{Sb}_2(\text{S,Se})_3$ on (100) and (101) facets of CdS; (b) the vertical growth of $\text{Sb}_2(\text{S,Se})_3$ film on CdS surface after adding extra Cd in the hydrothermal system; and (c) schematic diagram showing the proposed synergistic crystal growth model as the Cd concentration increases.

FIG. 15 depicts (a) cross-sectional energy dispersive X-ray spectrometry (EDX) elemental mapping of $\text{Sb}_2(\text{S,Se})_3/\text{CdS}$ heterojunction; (b) EDX line scan across the junction; (c) local transmission electron microscopy (TEM) image at the junction. The corresponding HRTEM (The insets show the fast Fourier transform (FFT), inverse fast Fourier transform (IFFT), and simulated electron diffraction pattern in sequence) focused at (d) CdS side, and (e) $\text{Sb}_2(\text{S,Se})_3$ side; (f) schematic diagram showing the vertical growth of $(\text{Sb}_4\text{X}_6)_n$ ribbons on CdS surface

with exact crystallographic orientation relationship; (g) illustration (3D) shows the detailed bonding information between $\text{Sb}_2(\text{S,Se})_3$ and CdS ; and (h) schematic used for the calculation of atomic distance mismatches.

5 **FIG. 16** depicts XRD patterns of the CdS substrate collected before and after hydrothermal reaction. To expose the underlying electron transporting layer (ETL) after hydrothermal reaction, the sample was treated with KOH aqueous solution to chemically etch off the top $\text{Sb}_2(\text{S,Se})_3$ layer.

10 **FIG. 17** depicts the powder XRD pattern and Rietveld refinement for $\text{Sb}_2(\text{S,Se})_3$ powder. The sample was collected at the bottom of hydrothermal reactor.

FIG. 18 depicts (a) external quantum efficiency (EQE) curves; (b) the plots of $\Delta I_{\text{integrated}}(\text{Cell}_i\% - \text{Cell}_0\%)$ as a function of light wavelength extracted from the EQE; (c) light intensity-dependent V_{OC} ; (d) temperature dependent- V_{OC} of $\text{Sb}_2(\text{S,Se})_3$ solar cells prepared with different Cd concentration; (e) transient absorption spectra of $\text{hk1-Sb}_2(\text{S,Se})_3$ sample; and (f) transient kinetic trace showing the decay of hk0- and $\text{hk1-Sb}_2(\text{S,Se})_3$ sample monitored at 650 nm.

FIG. 19 depicts the transient absorption (TA) spectra of $\text{hk0-Sb}_2(\text{S,Se})_3$ sample recorded at 10, 100, 1000, 4000 ps after excitation.

FIG. 20 depicts (a) J-V curve of the best performing $\text{Sb}_2(\text{S,Se})_3$ solar cell device measured under AM 1.5G illumination, and (b) its EQE measurement; and (c) the corresponding cross-sectional scanning electron microscopy (SEM) image.

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Description

It has been surprisingly found that the epitaxial growth of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ can be accomplished through the use of a specific substrate material. Thus, in a first aspect of the invention, there is provided a method of forming a film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$, comprising the steps of:

- 30 (a) placing a substrate, comprising:
- a first layer formed from SnO_2 ; and
 - a second layer on top of the first layer, the second layer providing a surface for $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ growth, the second layer formed from CdS in hexagonal form, where the
- 35 surface is substantially formed from a (100) facet of the hexagonal CdS ,
against a wall of a vessel, such that the substrate is positioned at an angle relative to a base of the vessel;

(b) immersing the substrate in an aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ and conducting a hydrothermal reaction for a period of time at a temperature of from 100 to 150 °C to grow the film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ on the second layer of the substrate, wherein the precursor solution further comprises a cadmium (II) salt in an amount to provide a molar percentage of Cd relative to the amount of Sb ($n_{\text{Cd}}/n_{\text{Sb}}$) of from 1 to 5%; and x is from 0 to 1.

Without wishing to be bound by theory, it is believed that the addition of Cd into the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ may help to favour the growth of vertical $(\text{Sb}_4\text{X}_6)_n$ ribbons. That is, the addition of Cd into the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ unexpectedly assist in the epitaxial growth of the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ film.

In particular embodiments of the invention that may be mentioned herein the relationship of the second layer and the film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ to each other may be $(001)_d \parallel [001]_d \parallel (100)_s [210]_s$. Where “d” refers to the deposited $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ material (i.e. the epitaxially-grown $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ film) and “s” refers to the CdS layer on the substrate’s surface, onto which the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ epitaxial layer is deposited.

In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

When used herein the term “substantially” when referring to the hexagonal CdS that forms the second layer of the substrate, is intended to refer to the situation where at least 50% (e.g. 51 to 75%, such as from 52 to 57%, such as about 56.5%) of the second layer’s surface is formed from the (100) facet of the hexagonal CdS, as determined by the intensity of the peaks in the X-ray diffraction pattern. For example, in embodiments that may be mentioned herein, the hexagonal CdS may have (100) and (101) facets, amongst others, and the surface of the second layer may be formed from the (100) and (101) facets of the hexagonal CdS, where the ratio of intensity of the (100) facet to the (101) facet in the X-ray diffraction pattern is greater than or equal to 1.3.

Any suitable period of time may be used for step (b) of the method above. Examples of suitable periods of time that may be mentioned include, but are not limited to, from 1 to 10 hours, such as from 2 to 4 hours, such as about 3.5 hours. Any suitable temperature may be used for step (b) of the method above. Examples of suitable temperature ranges that may be mentioned include, but are not limited to, from 120 to 150 °C, such as from 125 to 130 °C. Without wishing to be bound by theory, it is believed that keeping the temperature of the deposition step low (e.g. less than or equal to 150 °C, such as less than or equal to 130 °C), can prevent the formation of randomly oriented grains ascribed to randomness in the nucleation stage of the growth of the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ film on the CdS second layer.

The product obtained in step (b) of the above method may be used as-is or it may be subjected to a further post-formation annealing step. For example, the the product of step (b) of the method above may be annealed at a temperature of from 250 to 400 °C, such as from 300 to 350 °C, such as about 335 °C for a period of from 5 minutes to 1 hour, such as from 10 to 40 minutes, such as from 15 to 30 minutes, such as about 20 minutes. This further annealing (e.g. in a tube furnace) may be conducted to further enhance the crystallinity of the deposited epitaxial film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$.

As will be appreciated, in the formula $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$, if x is 0 then the product will be Sb_2Se_3 , while if x is 1 then the product will be Sb_2S_3 , and if x is 0.5, then the product will be $\text{Sb}_2\text{S}_{1.5}\text{Se}_{1.5}$. Other values can be worked out accordingly.

Any suitable aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ may be used in the method disclosed herein. For example, the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ may comprise $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 3\text{H}_2\text{O}$ and one or both of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and $\text{SeC}(\text{NH}_3)_2$. As will be appreciated, if only $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is present, then the product will be Sb_2S_3 , while if only $\text{SeC}(\text{NH}_3)_2$ is present, then the product will be Sb_2Se_3 . As such, in some embodiments of the invention that may be mentioned herein, the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ may comprise $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, but not $\text{SeC}(\text{NH}_3)_2$.

In particular embodiments of the invention, the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ may have a molar ratio of Sb:S of from 1:2 to 1:5 (e.g. about 1:4.8) and a molar ratio of Sb:Se of from 1:0 to 1:0.3 (e.g. about 1:0.24).

In particular embodiments of the invention, the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ may comprise a cadmium (II) salt in an amount ($n_{\text{Cd}}/n_{\text{Sb}}$) of from 1 to 4%, such as from 2 to

3.5%, such as from 2.5 to 3.25%, such as about 3%. As noted hereinbefore, the term " (n_{Cd}/n_{Sb}) " is intended to refer to the molar percentage of Cd relative to the amount of Sb.

Any suitable cadmium (II) salt may be used as the additive in step (b) of the method above.

- 5 For example, the cadmium (II) salt may be $CdSO_4$ or it may have the formula CdX_2 , where each X is a halide or NO_3 , optionally wherein X is I, Br or, more particularly, Cl. In particular embodiments of the invention that may be mentioned herein, the cadmium (II) salt may be $CdCl_2$.
- 10 As noted herein, the substrate is positioned at an angle relative to a base of the vessel so as to avoid precipitates from setting onto the CdS surface. Any suitable angle that enables the growth of the $Sb_2(S_xSe_{1-x})_3$ film may be used. For example, the angle may be from 20 to 60°, such as about 40°.
- 15 As will be appreciated, the substrate is placed such that the surface for $Sb_2(S_xSe_{1-x})_3$ growth (i.e. the surface substantially formed from a (100) facet of hexagonal CdS) faces towards the base of the vessel. In other words, the surface onto which an $Sb_2(S_xSe_{1-x})_3$ is to be grown faces the base of the vessel.
- 20 The substrate used in the method above may be formed by the steps of:
(bi) providing a precursor substrate comprising a first layer of SnO_2 and a second layer formed from CdS; and
(bii) coating a C_1 to C_3 alcohol solution of an oversaturated cadmium (II) salt for a first period of time on the precursor substrate to provide an intermediate substrate, which is then
25 annealed for a second period of time at a temperature of from 350 to 500 °C.

- When used herein, the term "a solution of oversaturated cadmium (II) salt" refers to a methanol solution having a concentration of from 0.9 to 0.11 M (e.g. from 0.10 to 0.11 M, such as about 0.109 M) of a cadmium (II) salt. Any suitable cadmium (II) salt may be used in the solution of
- 30 an oversaturated cadmium (II) salt. For example, cadmium (II) salt may be $CdSO_4$ or it may have the formula CdX_2 , where each X is a halide or NO_3 , optionally wherein X is I, Br or, more particularly, Cl. In particular embodiments of the invention that may be mentioned herein, the cadmium (II) salt may be $CdCl_2$. For example, the oversaturated solution may be prepared by dissolving 0.02g $CdCl_2$ in 1 mL methanol, since the solid cannot be fully dissolved at room
35 temperature (25 °C), this process was conducted by alternative using heat and ultrasonic dispersion. It should be noted that the recrystallization of $CdCl_2$ will occur when the solution is removed from heat, so the fully solvated solution should be used within 20 minutes, otherwise

it will be necessary to re-do the heating step before its use. Any suitable C_1 to C_3 alcohol may be used alone or in combination (e.g. methanol, ethanol, n-propanol, i-propanol). For example, the C_1 to C_3 alcohol may be methanol.

- 5 Without wishing to be bound by theory, it is believed that the combination of the use of an oversaturated cadmium (II) salt followed by annealing at a high temperature (e.g. in air) results in a CdS layer with enhanced crystallinity. In addition, it is believed that these steps provide a CdS layer that is hexagonal and has strongly preferential orientations of (100) and (002).
- 10 As noted above, the annealing step may help to enhance the crystallinity of the CdS layer. This annealing step may be conducted for any suitable period of time (e.g. of from 5 to 20 minutes, such as about 10 minutes) and for any suitable period of time (e.g. of from 400-420 °C, such as 415 °C).
- 15 The precursor substrate used to form the substrate used in the method disclosed herein may be formed by the steps of:
 - (di) providing a SnO_2 substrate comprising a surface formed by SnO_2 ; and
 - (dii) immersing the SnO_2 substrate in a CdS precursor solution at a temperature of from 45 to 100 °C for a period of time to form the precursor substrate.

- 20 As will be appreciated, the resulting material made by the process described herein may be particularly suited for use in the formation of a light absorbing device. As such, the SnO_2 substrate referred to above may further comprise an electrode layer. This electrode layer may be any formed from any suitable material. For example, the electrode layer may be formed from ITO glass or, more particularly, FTO glass.
- 25

- 30 In the method of forming the precursor substrate, any suitable period of time may be used for step (dii). For example, the period of time may be from 10 to 20 minutes, such as about 15 minutes. Additionally, any suitable temperature may be used for step (dii). For example, the temperature may be from 60 to 80 °C, such as about 65 °C.

- The SnO_2 substrate discussed above may be formed by the steps of:
 - (fi) providing a blank substrate material having a surface; and
 - (fii) spin-coating the surface of the blank substrate with a solution comprising SnO_2 nanoparticles to provide the SnO_2 substrate. In particular embodiments of this formation, one or more of the following may apply:
- 35

(gi) the SnO_2 nanoparticles may have a diameter of from 1 to 20 nm, such as from 3 to 4 nm;

(gii) the SnO_2 substrate obtained in step (fii) above may be subjected to annealing for a period of time at an elevated temperature. For example, the period of time may be from 10 minutes to 1 hour, such as about 30 minutes, and the elevated temperature may be from 100 to 200 °C, such as about 150 °C;

(giii) the spin-coating in step (fii) above may be conducted at a speed of from 1000 to 3500 rpm for a period of time, optionally wherein the speed is about 2500 rpm and/or the period of time is about 30 seconds.

As noted above, the resulting product if the method disclosed herein may be useful in a light absorbing device. As such, the method may further include placing a hole transport layer on the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ and placing an electrode on the hole transport layer. Any suitable hole transport layer and electrode may be used. For example, the hole transport layer may be spiro-OMeTAD and the electrode may be gold and/or silver (e.g. a layer of gold and/or silver that is from 30 to 100 nm thick, such as 60 nm thick).

In a second aspect of the invention, there is provided a light absorbing device comprising:

a first electron transport layer formed of SnO_2 ;

a CdS layer on the first electron transport layer as a second electron transport layer;

a $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer on the CdS layer as a light absorbing layer; and

a hole transport layer on the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer, wherein

the CdS layer is formed from CdS in hexagonal form, where the surface is substantially formed from a (100) facet of the hexagonal CdS and the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer is formed from a plurality of parallel $(\text{Sb}_4\text{X}_6)_n$ ribbons that extend from the CdS layer in a [001] direction.

Without wishing to be bound by theory, it is believed that the epitaxially-oriented $(\text{Sb}_4\text{X}_6)_n$ ribbons in the light absorbing device result in a device that displays a surprisingly improved power conversion efficiency. For example, light absorbing devices according to the current invention may display a power conversion efficiency of from 9.0 to 10%, such as about 9.24%.

As will be appreciated, the light absorbing device described herein can be formed using the methods described above.

The relationship between the CdS layer and the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer to each other may be $(001)_d [001]_d \parallel (100)_s [210]_s$, where “s” refers to the “substrate” layer (i.e. the CdS layer) and “d” refers to the “deposited” layer (i.e. the epitaxial layer of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$).

- 5 As will be appreciated, the light absorbing device will benefit from the inclusion of electrodes. As such, the first electron transport layer formed of SnO_2 may be attached to an electrode. More specifically, the first electron transport layer formed of SnO_2 will have a first surface and a second surface, where the first surface may be attached to a transparent electrode material and the second surface may be attached to the CdS layer. As noted above, in such
- 10 arrangements, the SnO_2 layer may be formed on the surface of the transparent electrode material. Any suitable transparent electrode material may be used. Examples include, but are not limited to ITO glass and FTO glass. In certain embodiments of the invention that may be mentioned herein, the transparent electrode material may be FTO glass.
- 15 In addition to an electrode layer being attached to the first electron transport layer, a further electrode layer may be attached to the hole transport layer. Thus, in embodiments that may be mentioned herein, the hole transport layer has a first surface attached to the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer and a second surface that may be attached to an electrode material. This electrode material may be a layer of gold and/or silver (e.g. gold). This electrode material may have any
- 20 suitable thickness, such as from 30 to 100 nm thick, such as 60 nm thick).

As noted above, the CdS layer is formed from CdS that has a hexagonal form. This hexagonal CdS has a number of facets, which include the (100) and (101) facets. The surface of the second electron transport layer may be formed from the (100) and (101) facets of the

25 hexagonal CdS. As noted above, the ratio of intensity of the (100) facet to the (101) facet in the X-ray diffraction pattern of the surface of the second electron transport layer may be greater than or equal to 1.3.

The hole transport layer may be any suitable hole transport layer material. For example, the

30 hole transport layer may be an organic semiconductor or an inorganic semiconductor with p-type conductivity. In particular embodiments of the invention, the hole transport layer may be selected from one or more of the group consisting of P3HT, PbS, MnS, CuSCN, and spiro-OMeTAD. In more particular embodiments of the invention, the hole transport layer may be spiro-OMeTAD.

As noted above, the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer is formed by a plurality of $(\text{Sb}_4\text{X}_6)_n$ ribbons. The plurality of $(\text{Sb}_4\text{X}_6)_n$ ribbons may be oriented in (hk1) planes. For example, the $(\text{Sb}_4\text{X}_6)_n$ ribbons display one or more (hk1) planes selected from (101), (111), (211) and (221).

- 5 In certain embodiments of the invention one or more of the following may apply:
- the (101) plane has a texture coefficient of greater than or equal to 1.80;
 - the (111) plane has a texture coefficient of greater than or equal to 1.20;
 - the (211) plane has a texture coefficient of greater than or equal to 1.10; and
 - the (221) plane has a texture coefficient of greater than or equal to 1.10.

10

Without wishing to be bound by theory, it is believed that the unique 1D crystal structure of the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ film (e.g. $\text{Sb}_2(\text{S},\text{Se})_3$ film) obtained by the method hereinbefore discussed leads to the anisotropic electrical properties disclosed herein. This is believed to be because the charge transport along the $(\text{Sb}_4\text{X}_6)_n$ ribbon is much faster than in other directions, which means

15 that the performance of devices based on $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ film (e.g. $\text{Sb}_2(\text{S},\text{Se})_3$) obtained by the method disclosed herein can be enhanced by utilizing the vertically oriented $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ (e.g. $\text{Sb}_2(\text{S},\text{Se})_3$) light absorber layer due to the efficient charge transport and less defects concentration caused by the regularly arranged grains. This enables the application of the material in photovoltaics and in a photoelectrochemical system.

20

Application in photovoltaics: It has been reported that the world record efficiency of $\text{Sb}_2(\text{S},\text{Se})_3$ solar cell has achieved 10% recently, which make it a research hotspot and closer for commercial production as the theoretical power conversion efficiency can be up to 32%. However, a careful study found that the preferred orientation of the reported $\text{Sb}_2(\text{S},\text{Se})_3$ films

25 generally had a preferred orientation of (hk0), which inevitably decrease the charge transport efficiency in the solar cell devices (see R. Tang, *et. al.*, *Nat. Energy*, 2020, **5**, 587-595.). It is believed that the power conversion efficiency of $\text{Sb}_2(\text{S},\text{Se})_3$ can be further enhanced by using the techniques disclosed herein. This is further detailed herein and in the examples below. As will be appreciated, the light absorbing devices described in the second aspect of the invention

30 are suitable for use in photovoltaic applications.

Application in a photoelectrochemical system: Solar hydrogen production can also be accomplished by a photoelectrochemical system, which simultaneously functions as a light harvester and electrolyzer. Yang et al. demonstrated a highly efficient photoelectrochemical

35 water splitting system based 1D Sb_2Se_3 by adjusting the anisotropic structure. The high photocurrent generated in the best performing Sb_2Se_3 device is explained by an appropriately [221]-oriented nanostructure array, in which tilted $[\text{Sb}_4\text{Se}_6]_n$ ribbons are vertically stacked on

the substrate. The electronic carrier could be easily transported to the vertical direction through the covalently bonded ribbons (see W. Yang, *et. al.*, *Adv. Energy Mater.*, 2018, **8**, 1702888.). It is believed that vertically oriented $\text{Sb}_2(\text{S,Se})_3$ has great advantages acting as the photocathode for hydrogen production through a photo-assisted electrochemical (PEC) water splitting system, which would greatly increase the photocurrent density due to faster charge transport efficiency. It is noted that the devices discussed in relation to the second aspect of the invention above can be used as a photoelectrode to generate hydrogen by a photo-assisted electrochemical water splitting reaction. More particularly, the same (or similar) devices disclosed in the examples section below may be used as a photoelectrode to generate hydrogen by a photo-assisted electrochemical water splitting reaction.

Further aspects and embodiments of the invention will now be described by reference of the following non-limiting examples.

Examples

Materials

SnO_2 nanoparticle solution was purchased from Alfa Aesar (LOT: 44592). The etched FTO glass was purchased from Advanced Election Technology CO.,Ltd. Spiro-OMeTAD from ,acetone, isopropanol, ethanol, CdSO_4 , thiourea, $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 3\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{SeC}(\text{NH}_2)_2$, Spiro-OMeTAD, chlorobenzene, 4-tert-butyl pyridine, Li-TFSI from Sigma-Aldrich.

Analytical techniques

XRD

The crystal structure of $\text{Sb}_2(\text{S,Se})_3$ thin film was examined using XRD (Bruker D8 Advance) with Cu-K α radiation (1.5406 Å). The lattice parameters of mixed $\text{Sb}_2(\text{S,Se})_3$ were calculated from high-precision XRD profiles using the Rietveld method which was conducted by TOPAS V6 software (The fundamental parameter (FP) approach was used as the profile shape function). To acquire the crystallographic information of nanocrystalline CdS, GIXRD was performed at an incidence angle of 0.5° .

Field emission scanning electron microscopy (FE-SEM)

The cross-sectional morphologies were collected by FE-SEM (JOEL JSM-7600F).

Atomic force microscope (AFM)

The surface morphologies of CdS substrate were collected by AFM (Asylum research MFP3D).

TEM

The microstructure information of $\text{Sb}_2(\text{S,Se})_3$ and CdS were acquired by (JEOL 2100F).

5 *EDX*

The distribution of elements on the interface was collected by Oxford INCA attached to TEM.

Focus ion beam system

10 The cross-section sample was prepared by focus ion beam system (FIB, ZEISS Crossbeam 540). The corresponding simulated electron diffraction patterns used for indexing were obtained by JEMS software.

Example 1. Preparation of $\text{Sb}_2(\text{S,Se})_3$ solar cell device

15 According to the thin film epitaxial growth theory, the final orientation of target material is primarily determined by the orientation of initial seeds, so we began by controlling the facets of CdS matrix to regulate the nucleation process of $\text{Sb}_2(\text{S,Se})_3$. In addition, the crystal orientation of $\text{Sb}_2(\text{S,Se})_3$ films was controlled via a facile solution process. The strategy is built upon a synergistic crystal growth mechanism that utilizes the minimum energy principle to
20 induce the formation of favorable nucleation sites of underlying ETL, which in turn renders the in-situ deposition of (hk1)-oriented $\text{Sb}_2(\text{S,Se})_3$ absorber layer. The complete fabrication procedure of the $\text{Sb}_2(\text{S,Se})_3$ device 100 is illustrated in FIG. 3a, in which a superstrate configuration of FTO/SnO₂/CdS/ $\text{Sb}_2(\text{S,Se})_3$ /Spiro-OMeTAD/Au was sequentially assembled. The $\text{Sb}_2(\text{S,Se})_3$ device 100 includes FTO 110, SnO₂ 111, CdS 112, $\text{Sb}_2(\text{S,Se})_3$ 113, Spiro-
25 OMeTAD 114, and Au 115. A post-treatment using CdCl₂ solution was performed to enhance the crystallinity of CdS ETL prepared by CBD process. In addition, an extra amount of Cd was intentionally added during the hydrothermal process to control the nucleation stage of $\text{Sb}_2(\text{S,Se})_3$.

30 *Preparation of $\text{Sb}_2(\text{S,Se})_3$ solar cell device*

Prior to the depositions, etched FTO glass (1.5 cm by 2 cm) was ultrasonically cleaned in acetone, isopropanol and ethanol for 30 min each and treated with UV ozone for 15 min. Then, a thin film of SnO₂ was spin-coated on the glass using a commercial suspension of SnO₂ nanoparticle (3–4 nm) solution (15% in H₂O, and 60 μl used in each cycle) at 3000 rpm for 30
35 s, followed by annealing at 150 °C for 30 min in air. The SnO₂ film acts as a buffer layer to change the nucleation and growth of CdS. The CdS ETL was prepared through chemical bath deposition method. This was carried out in an open aqueous system containing of CdSO₄ (25

ml, 15mM), thiourea (12.5 ml, 1.5M), aqueous ammonia (32.6 ml) and DI water (183 ml) at a reduced holding temperature of 65 °C for 9, 10, 11, 12, 13, 14, 15, or 16 min, to ensure the formation of homogeneous and pin-hole film. In order to enhance the crystallinity, the as-prepared CdS nanocrystalline film was treated with oversaturated CdCl₂ solution and annealed at an optimized temperature of 415 °C for 10 min.

The Sb₂(S,Se)₃ light absorber layer was fabricated by a hydrothermal process. The CdS substrate prepared was transferred into a Teflon container and tilted against the wall at an angle. The precursor solution composed of K₂Sb₂(C₄H₂O₆)₂·3H₂O (0.95 g, 15.9m%), Na₂S₂O₃·5H₂O (1.70 g, 76.45m%), SeC(NH₂)₂ (0.085 g, 7.65 m%) and deionised (DI) water (100 ml). To control the preferred orientation of absorber layer, a specific amount of CdCl₂ (molar ratio of Cd to Sb (n_{Cd}/n_{Sb}) = 0%, 1%, 2%, 3% or 4%; 5.25 mg (1%), 10.50 mg (2%), 15.75 mg (3%) or 21.00 mg (4%)) was added in the above solution. The reaction mixture was stirred at room temperature for about 15 s and then poured into the Teflon container. Hydrothermal reaction was carried out at a low temperature of 120 °C which can prevent the formation of randomly oriented grains ascribed to the randomness in the nucleation stage. After 3.5 h, the samples were taken out followed by washing with DI water and blow drying with compressed nitrogen. The as-deposited film was further annealed in a tube furnace to enhance its crystallinity. The tube was precleaned with nitrogen several times. The annealing process was conducted at 335 °C for 20 min. For the deposition of spiro-OMeTAD, spiro-OMeTAD (36.6 mg) was first dissolved in a mixed solution containing chlorobenzene (1 mL), 4-tert-butyl pyridine (28.8 µL) and Li-TFSI solution (18.8 µL, 520 mg mL⁻¹ Li-TFSI in acetonitrile). The as-prepared spiro-OMeTAD solution was spin-coated onto the Sb₂(S,Se)₃ sample at 2500 rpm for 30 s. To complete the device fabrication, a 60-nm-thick Au electrode was deposited by thermal evaporation. After the base pressure reaching below 5*10⁻⁴ Pa, the heating current was adjusted carefully so as to reach a deposition rate of 0.01 nm/s for the first 10 nm thickness, and then increased to achieve a deposition rate of 0.06 nm/s for the rest 50 nm.

Example 2. Characterization and performance of device

Device performance test

The power conversion efficiency of solar cell device was obtained by I-V test in reverse scan mode, which was performed using a solar simulator (AM1.5), the starting and ending scan voltage were set to be -0.1 V and 1.2 V, respectively.

Results and discussion

The deposition of CdS film was inter-linked with the subsequent Cd addition process and that these two processes together determine the final device performance. As shown in FIG. 3b, efficient devices with power conversion efficiency (PCE) > 8% were only located within a specific region on the efficiency contour map: a CdS deposition time of ~11–13 min and Cd concentration of ~0.75–1.5%. Looking along the vertical axes, either too long or too short of a time for CdS deposition resulted in poor device performance, which can be interpreted from the perspective of the growth characteristics of CdS. It has been widely reported that the deposition of CdS film during CBD process follows the cluster-by-cluster film growth mode at higher reaction temperature (H. Moualkia *et al.*, *J. Phys. D: Appl. Phys.* **2009**, 42, 135404). Hence, a short deposition time gives rise to a porous film, thus causing deteriorated device performance due to circuit shunting. On the other hand, prolonged deposition time caused an increase in the film thickness (FIG. 4a). However, a thicker CdS window layer leads to strong parasitic absorption in the 300–520 nm range and increased series resistance, inevitably resulting in a low J_{SC} , which is a common issue for chalcogenide-based photovoltaics (J. Y. Cho *et al.*, *J. Mater. Chem.* **2020**, 8, 20658-20665; and Z. Rong *et al.*, *Adv Funct. Mater.* **2019**, 29, 1904018).

FIG. 5 shows the variations of the device parameters with increasing Cd concentration in the hydrothermal solution while fixing the deposition time of CdS film at the optimum value of 12 min. It can be seen in FIG. 5 that as the concentration of Cd^{2+} increases from 0% to 5%, a monotonic increase in V_{OC} is observed, while J_{SC} first increases followed by a decreasing trend. Finally, 1% Cd yields the maximum PCE beyond 9%, which is 25% performance improvement compared to the pristine $Sb_2(S,Se)_3$ device. In view of the same experimental conditions except for the modified hydrothermal synthesis parameters, the underlying reasons for enhanced device performance can be elucidated from the relationships between structure-property-performance of $Sb_2(S,Se)_3$ layer. FIG. 6 shows the XRD patterns of annealed $Sb_2(S,Se)_3$ thin films deposited with different Cd concentrations. It is apparent that the crystal structure of mixed-anion $Sb_2(S,Se)_3$ follows that of the orthorhombic Sb_2S_3 (JCPDS #42-1393, space group: Pbnm). Only a slight peak shift towards smaller angle was observed due to the incorporation of larger Se^{2-} ions. For pristine $Sb_2(S,Se)_3$ film without any Cd, the film was dominated by (hk0)-oriented grains, indicating the horizontal growth of $(Sb_4X_6)_n$ ribbons. As mentioned above, this is thermodynamically favorable since film growth along the preferred (hk0) orientations can minimize the total free energy of the crystals. Interestingly, this situation changed significantly when additional Cd was incorporated into the hydrothermal reaction system. The amount of Cd was found to precisely govern the growth of crystals with certain orientations. The main XRD reflections of $Sb_2(S,Se)_3$ film gradually transformed from (hk0) to (hk1) planes such as (101), (211) and (221) with increasing the Cd content from 1% to 4%.

The corresponding texture coefficients (TC) of the main diffraction peaks were also calculated as shown in FIG. 3c. The (hk0) and (hk1) facets show opposite trend as Cd content increases, suggesting the preferential vertical growth of $(\text{Sb}_4\text{X}_6)_n$ ribbons after adding extra Cd (FIG. 3c). It should be noted that no distinguishable difference was detected in terms of peak positions with varying Cd concentration. The exact lattice parameters and interplanar spacing for the mixed-anion $\text{Sb}_2(\text{S,Se})_3$ were refined through Pawley method (FIG. 7), and the results are summarized in Tables 1 and 2. For convenience, $\text{Sb}_2(\text{S,Se})_3$ fabricated with and without Cd will be henceforth referred to as hk1- $\text{Sb}_2(\text{S,Se})_3$ and hk0- $\text{Sb}_2(\text{S,Se})_3$, respectively.

Table 1. Lattice parameters of hk1- and hk0- $\text{Sb}_2(\text{S,Se})_3$ films refined by Pawley method.

Parameters	Sb_2S_3 (Standard)	hk1- $\text{Sb}_2(\text{S,Se})_3$	hk0- $\text{Sb}_2(\text{S,Se})_3$
a	11.25	11.286	11.288
b	11.33	11.409	11.415
c	3.83	3.855	3.861
Cell volume ($\text{\AA}^3$)	488.18	496.42	497.54
R-Bragg	--	0.502%	0.406%
R_{wp}	--	10.05%	8.6%
GOF	--	2.39	2.04

Table 2. The refined interplanar spacing of hk1- $\text{Sb}_2(\text{S,Se})_3$ film.

2 θ	hkl	d($\text{\AA}$)	I	2 θ	hk	d($\text{\AA}$)	I	2 θ	hk	d($\text{\AA}$)	I
11.0	11	8.02	0.27	39.2	04	2.29	19.	49.9	02	1.82	5.3
15.5	02	5.70	2.41	39.6	34	2.27	2.4	50.5	12	1.80	16.
15.6	20	5.64	0.40	39.7	43	2.26	2.9	52.5	35	1.74	24.
17.4	12	5.09	7.86	40.1	14	2.24	26.	52.6	22	1.73	5.
17.5	21	5.05	0.017	40.2	15	2.23	10.	52.7	53	1.73	10.
22.1	22	4.01	3.95	40.3	41	2.23	0.61	53.7	06	1.70	48.
24.3	10	3.64	16.4	40.7	51	2.21	0.77	53.8	13	1.70	31
24.6	13	3.60	16.2	41.0	33	2.19	2.9	53.9	36	1.69	14.
24.9	31	3.57	15	42.7	25	2.11	23.	54.8	61	1.67	10.
25.6	11	3.47	11.3	43.0	52	2.09	10.	55.8	23	1.64	21.
27.9	02	3.19	15	45.1	44	2.00	5.4	56.7	62	1.62	2.4
28.2	23	3.15	13.6	46.3	34	1.95	4.8	57.1	45	1.61	1.7
28.4	32	3.14	7.04	46.4	43	1.95	32.	57.2	54	1.60	2.3
29.0	12	3.07	6.93	46.5	35	1.95	18.	57.8	40	1.59	1.4
29.1	21	3.06	57.3	46.5	50	1.94	12.	58.4	46	1.57	1.3
32.1	22	2.78	79.4	46.9	15	1.93	21.	58.5	41	1.57	2.
33.2	30	2.69	34.6	47.1	00	1.92	66.	58.7	64	1.57	1.6
34.0	13	2.63	1.06	47.8	06	1.90	6.2	58.9	27	1.56	3.3
34.1	31	2.62	14.2	48.3	60	1.88	5.0	59.0	33	1.56	3.0

35.2	24	2.54	25.6	48.5	11	1.87	2.7	59.4	36	1.55	10.
35.4	42	2.52	4.69	49.0	61	1.85	7.1	59.8	63	1.54	8.0
36.7	23	2.44	17.9	49.4	52	1.84	0.81	60.1	24	1.53	41.

It was noticed that when more Cd (>1%) was added into the hydrothermal reaction, the J_{SC} of the devices decreased dramatically even if stronger [hk1] reflections could be detected from the film, resulting in a deteriorated performance instead. This phenomenon was attributed to the increased parasitic absorption from CdSe layer with smaller band gap subjected to the poisoning effect of Se.

Example 3. Key role of CdS in $Sb_2(S,Se)_3$ solar cells

Most of the high efficiency $Sb_2(S,Se)_3$ solar cells are reported on devices with n-i-p architecture which ensures efficient charge separation and injection to the electron and hole transport layers (R. Tang *et al.*, *Nat. Energy* **2020**, 5, 587-595; X. Wang *et al.*, *Adv. Energy Mater.* **2020**, 10, 2002341; and C. Jiang *et al.*, *Energy Environ. Sci.* **2021**, 14, 359-364). In terms of electron transporting material, two types of compounds are widely employed, namely, binary oxides (TiO_2 , SnO_2) and sulfides (CdS, ZnS). The point to emphasize here is that the ETL serves a dual role in $Sb_2(S,Se)_3$ device: it not only promotes the separation of charge carriers by forming a heterojunction with the absorber layer, but also acts as the growth matrix that directly influences the quality of $Sb_2(S,Se)_3$ film. In the case of oxide ETL, a weak orientating effect on $Sb_2(S,Se)_3$ is usually observed because of the large lattice mismatch. Thus, a rapid crystallization process is generally needed to avoid the poor polycrystalline film quality originating from the undesired free grain growth (X. Wang *et al.*, *Nanoscale* **2017**, 9, 3386-3390). In comparison, sulfides generally have small lattice mismatch and can bond better with $Sb_2(S,Se)_3$, which allows a slow growth rate (up to several hours) to obtain remarkably smooth and homogeneous films (X. Jin *et al.*, *Adv. Funct. Mater.* **2020**, 30, 2002887; and W. Wang *et al.*, *Adv. Electron. Mater.* **2019**, 5, 1800683). Hence, it was hypothesized that the grain orientation can be controlled by tuning the nucleation/growth condition. To verify the hypothesis, AES depth profiling with high sensitivity and spatial resolution was first utilized to locate the elemental distribution across the film thickness.

Elemental depth profiling

Elemental depth profiling was conducted using AES (accelerating voltage of 10 KeV and probe current of 10 nA) equipped with Ar^+ ion beam sputtering (AES, JEOL JAMP-7830F). XPS was conducted on the Kratos AXIS Supra instrument equipped with a monochromatic Al K α

(1486.7 eV) X-ray source. The sputtering was done with Ar Gas Cluster Ion Source (GCIS, Kratos Analytical Inc. Minibeam 6) operated at 10 keV Ar_{1000}^+ .

To calculate the elemental ratio, the XPS peaks belonging to the relative elements were integrated separately to obtain the peak area S . Then, the atomic ratio was calculated by using the following equation:

$$\frac{A}{B} = \frac{S_A/RSF_A}{S_B/RSF_B}$$

Where RSF is the relative sensitivity factor ($RSF_S = 0.668$, $RSF_{Se} = 0.853$ and $RSF_{Sb} = 8.627$ for Kratos instrument).

DFT calculation parameters

The electronic structures and adsorption free energy were computed by Vienna ab initio Simulation package (VASP) of DFT. The projector augmented wave (PAW) model with Perdew–Burke–Ernzerhof (PBE) function was employed to describe the interactions between core and electrons, and an energy cutoff of 450 eV was used for the planewave expansion of the electronic wave function. The Brillouin zones of all systems were sampled with gamma-point centered Monkhorst–Pack grids. $9 \times 9 \times 5$, $8 \times 5 \times 1$, $5 \times 5 \times 1$, $4 \times 8 \times 1$, $4 \times 3 \times 1$ Monkhorst Pack k-point setup were used for slab geometry optimization. The force and energy convergence criterion were set to $0.02 \text{ eV } \text{\AA}^{-1}$ and 10^{-5} eV , respectively.

Calculation of Gibbs free energy change

The calculation of Gibbs free energy change was performed by HSC Chemistry (T.J. Sianga *et al.*, Energy **2020**, 198, 117394)

Results and discussion

As presented in FIG. 8, Sb profiles in both $\text{hk0-Sb}_2(\text{S,Se})_3$ and $\text{hk1-Sb}_2(\text{S,Se})_3$ films are almost identical, showing a flat profile throughout the bulk of absorber layer. On the other hand, S intensity gradually increases from bottom to top, while more Se is observed at the absorber/ETL interface. These results suggest that Se^{2-} is more active compared to S^{2-} in reacting with Sb^{3+} and thus dominated the initial reactions, which has been validated by the calculation of Gibbs free energy change (ΔG) as a function of temperature (FIG. 9). Cd was detected only at the absorber/ETL interface for both films but revealed different distribution behaviors. For $\text{hk0-Sb}_2(\text{S,Se})_3$, the Cd peak is asymmetric with shallower gradient at the CdS/ SnO_2 interface, which is an indication of rough CdS surface, as shown in the inset of FIG. 8. In sharp contrast, the $\text{hk1-Sb}_2(\text{S,Se})_3$ film displays a symmetric Cd peak shape, which is

the typical feature of the signals coming from a relatively flat film, as shown in the inset of FIG. 8.

We further utilized XPS to verify the chemical states of the elements of interest at different positions from the sub-surface to the bottom of $\text{Sb}_2(\text{S,Se})_3$ with the help of Ar^+ sputtering. As can be seen in FIG. 10, the measured S 2p and Se 3d core-levels from hk0- $\text{Sb}_2(\text{S,Se})_3$ and hk1- $\text{Sb}_2(\text{S,Se})_3$ films are almost identical and no signal from Cd is detected. In addition, quantitative XPS analysis also confirms the presence of S/Se vertical gradients in both $\text{Sb}_2(\text{S,Se})_3$ films (FIG. 10d), in good agreement with the AES results. According to the above analysis, it was concluded that the added Cd has been completely reacted by S^{2-} during the initial heating stage, forming fresh CdS. Furthermore, the generated CdS species is supposed to occupy the bottom $\text{Sb}_2(\text{S,Se})_3/\text{ETL}$ interface, which makes the final film flat and smooth.

The above conclusion is reasonable if the growth behavior of CdS is taken into account. For photovoltaic applications, binary compound CdS is usually fabricated by the CBD process which can guarantee high film quality. It is well known that CdS can exist as both metastable cubic phase and stable hexagonal phase. Studies have indicated that the structure of the CBD-CdS films depends strongly on the type of the substrate. In the inventors' previous work (X. Jin *et al.*, *Adv. Funct. Mater.* **2020**, 30, 2002887), the as-prepared CdS on thin TiO_2 buffer layer was found to have a hexagonal structure with dominant facets of (100) and (002) after annealing at 400 °C for 7 min. The (002) facet was experimentally confirmed to be detrimental for the vertical growth of $(\text{Sb}_4\text{X}_6)_n$ ribbons due to the polar surface. It is believed that the desired (100) of CdS substrate can be further strengthened by further optimizing some processing parameters, such as annealing temperature and time, which facilitate the vertical growth of $\text{Sb}_2(\text{S,Se})_3$. Nevertheless, there is a large tolerance even if the unwanted (002) facet appeared. However, as extra Cd was added during the hydrothermal process, at least some of the unwanted (002) facets were transformed into the (100) facet through a surface reconstruction process, thereby guaranteeing the subsequent vertical growth of $\text{Sb}_2(\text{S,Se})_3$ layer.

Considering that the heterogeneous nucleation/growth during hydrothermal process has the quasi-epitaxial feature, we resorted to exposing specific facets of CdS to modify the initial nucleation environment for the anchoring of $(\text{Sb}_4\text{X}_6)_n$ ribbons. We found that by replacing TiO_2 with SnO_2 nanoparticle film and employing an optimized thermal treatment strategy, high-quality hexagonal CdS substrate with ideal exposed facets can be obtained. FIG. 11a shows the GIXRD of CdS substrate after thermal treatment. The two strong diffraction peaks at 24.8°, 28.2° and a relatively weak peak at 43.6° were indexed to the (100), (101) and (110) planes of hexagonal CdS, respectively. The weak peak between (100) and (101) originates from the

FTO substrate based on the incident angle dependent GIXRD analysis (FIG. 4b). In addition, the grain size of the heat-treated CdS film increases significantly compared with the as-deposited CdS, as revealed by AFM (FIG. 11c-d), indicating an enhanced crystallinity of ETL, and thus high-quality heterojunction could be formed.

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From a crystallographic perspective, Cd and S atoms have totally different stacking sequences in the directions perpendicular to (100) and (101) planes. As can be seen in FIG. 12, S and Cd are evenly distributed on {100} planes, making it a nonpolar surface. In contrast, the {101} plane is a polar surface with the positively-charged Cd layer and negatively-charged S layer arranged alternately along the [101] direction. For crystal growth, however, the opposite polarity of the planes represents different thermodynamic stability. To quantify this point, the surface energy (γ) of the (101), (100), (002) and (110) facets was calculated using DFT (FIG. 13). As shown in FIG. 11b, $\gamma_{(002)}$ and $\gamma_{(101)}$ are nearly six and two times larger than $\gamma_{(100)}$, respectively. According to crystal growth theory, the growth rate of a specific crystal facet can be estimated from its surface energy. Generally, the morphologically important surfaces during the reaction are those with the slowest growth rate. Therefore, the (101) facet of CdS with larger surface energy possesses a high growth rate and will quickly disappear from the crystal surfaces.

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Based on the calculated surface energy, the crystal morphology of CdS under thermodynamic equilibrium state can be simulated according to Wulff construction method. As shown in the inset of FIG. 11b, CdS crystal tends to crystallize into cylindrical shape with umbrella-like ends, where the (100), (110) and (101) planes form a triangular configuration with three sharing edges and one sharing corner. Predictably, this initial morphology would undergo further evolution upon the introduction of additional Cd. Here, we need to understand that the crystal growth in the hydrothermal system is a joint result of kinetic and thermodynamic processes. Although the Sb, Cd, S and Se sources were dissolved in the precursor solution simultaneously, at the very beginning the available free cations would solely be Cd^{2+} because of the extremely slow release rate of Sb due to the strong chelate effect in antimony potassium tartrate. In this case, the reaction between Cd and S would dominate the initial heating stage. On the other hand, the reduction in the surface energy was considered to be the primary driving force for the film growth during this stage. Hence, eventually, CdS growth along the [101] direction proceeds until they merge and flatten the CdS surface along [100] direction (FIG. 14b). The flat CdS surface is confirmed by the more symmetrical profile of the Cd signal in the AES depth profile (FIG. 8) as well as the smoother surface after hydrothermal reaction as shown in FIG. 11d-e.

As the reaction temperature of the hydrothermal system continues to increase, more free Sb^{3+} ions are released and start to react with S^{2-} to form the initial seeds on top of the modified CdS. As shown in FIG. 14a, the (100) nonpolar facet of CdS favors the vertical anchoring of $(\text{Sb}_4\text{X}_6)_n$ ribbons by forming two dative bonds simultaneously, namely $\text{Cd}_{(\text{CdS})}-\text{X}_{(\text{Sb}_2(\text{S,Se})_3)}$ and $\text{S}_{(\text{CdS})}-\text{Sb}_{(\text{Sb}_2(\text{S,Se})_3)}$. In contrast, the polar (101) plane can only meet the requirement to form single bond at a time due to the alternately arranged mono-elemental layers of either S or Cd, which is thermodynamically unstable. In this scenario, the ribbon tends to lay flat on the CdS surface through weak van der Waals force to minimize the total surface energy.

10 Example 4. Synergistic crystal growth model

Combining the crystal growth characteristics of CdS and $\text{Sb}_2(\text{S,Se})_3$, a synergistic crystal growth model was proposed to describe the formation and structural evolution of the vertically oriented $\text{Sb}_2(\text{S,Se})_3$ film during hydrothermal process.

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Chemically etching of the $\text{Sb}_2(\text{S,Se})_3$ layer

The chemically etching of $\text{Sb}_2(\text{S,Se})_3$ layer was conducted by wiping the surface with KOH solution-wetted cotton swab.

20 Results and discussion

From the results in Example 3, it is clear that the added Cd^{2+} will first react with S^{2-} preferentially on the high-energy (101) facets of CdS substrate, thus exposing more (100) facets in the lateral dimension due to the shrinking of side (101) plane (FIG. 14b). More importantly, the polarity of CdS surface directly determines the anchoring mode of $(\text{Sb}_4\text{X}_6)_n$ ribbons. Hence, one can easily understand that a random crystal growth behavior of $\text{Sb}_2(\text{S,Se})_3$ would happen on CdS surface when only Sb^{3+} and Se^{2-} ions are present in the solution, as shown in FIG. 14c. However, this situation was significantly modified after extra Cd was introduced. The transition of the nucleation sites effectively prohibited the potential horizontal growth of $(\text{Sb}_4\text{X}_6)_n$ ribbons and promoted their vertical growth at the same time. Thus, high quality $\text{Sb}_2(\text{S,Se})_3$ thin film with preferred (hk1) orientations can be formed with the help of the synergistic effect from Cd at the optimum Cd concentration. Higher Cd concentration above the threshold (3%) led to new conical CdS with {101} facets, resulting in the formation of horizontally oriented ribbons (FIG. 14c). This is also evidenced by the texture coefficients shown in FIG. 3c.

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Example 5. Crystallographic orientation relationship between absorber and substrate

To validate the proposed crystal growth model, the in-depth information about the interfacial microstructures of $\text{CdS}/\text{Sb}_2(\text{S,Se})_3$ contact was collected by performing HRTEM and EDX.

Results and discussion

FIG. 15a shows the TEM EDX elemental mapping for hk1- $\text{Sb}_2(\text{S,Se})_3$ sample. The observation of well-defined junction interface indicates the absence of heat-induced interdiffusion of Sb and Cd, suggesting good thermal stability of $\text{Sb}_2(\text{S,Se})_3$ and CdS during thermal annealing conditions. By means of local EDX line scan, precise elemental distribution across the heterojunction could be analyzed. As shown in FIG. 15b, the boundaries between substrate/ETL/absorber can be clearly distinguished. However, we noticed that there was an obvious extension of Se signal into the CdS region, which indicates that the Se ions may be involved in the reaction with Cd during the initial heating stage.

To verify that Se ions may be involved in the reaction with Cd during the initial heating stage, a separate sample was treated with alkaline solution to chemically etch off the top $\text{Sb}_2(\text{S,Se})_3$ layer, and then the retained “cleaned” ETL was used for XRD analysis. As shown in FIG. 16, the diffraction peaks corresponding to (100) and (101) planes of CdS have slightly shifted towards smaller angles, suggesting that the top surface of ETL existed in the form of $\text{CdS}_x\text{Se}_{1-x}$. In addition, Cd also seems to concentrate at the ETL/absorber interface thus confirming our earlier observation that minimal (or none) of it is incorporated in the $\text{Sb}_2(\text{S,Se})_3$ lattice. FIG. 15c shows the typical interfacial microstructure of $\text{Sb}_2(\text{S,Se})_3/\text{CdS}$ heterojunction in which a clear and smooth transition is formed by two distinct sets of well-ordered lattice fringes. For the CdS substrate side (FIG. 15d), the HRTEM image exhibits an interplanar distance of 0.357 nm, corresponding to the (100) plane of hexagonal CdS. The insets exhibit the corresponding FFT in reciprocal space and IFFT of lattice fringes with accompanying simulated electron diffraction (ED) pattern in sequence. The FFT image is characterized by a hexagonal pattern, matching well with the simulated ED pattern along the [001] zone axis. For the $\text{Sb}_2(\text{S,Se})_3$ side (FIG. 15e), the measured d-spacings of 0.316 and 0.362 nm can be indexed to the (320) and (101) planes of orthorhombic $\text{Sb}_2(\text{S,Se})_3$ (Table 2), respectively. The interplanar angle was determined to be 72.4° , in accordance with the theoretical value of 74.4° calculated from these two intersecting planes. Moreover, according to Weiss Zone law matches, the simulated ED pattern acquired from the [232] zone axis coincides with the obtained FFT image which is featured by parallelogram pattern, as shown in the inset of FIG. 15.

Based on the above information acquired from TEM study, the detailed chemical bonding at the absorber/ETL interface can be reconstructed with exact spatial orientation relationship as shown in FIG. 15f, wherein the [232] zone axis of $\text{Sb}_2(\text{S,Se})_3$ is parallel to the [001] zone axis

of CdS. The detailed in-plane bonding is illustrated in FIG. 15g and 12. The overlapped atomic site occupation between $\text{Sb}_2(\text{S,Se})_3$ and CdS proves the epitaxial growth of $\text{Sb}_2(\text{S,Se})_3$ on the (100) facet of hexagonal CdS substrate, which can be described as $(001)_d[001]_d\parallel(100)_s[210]_s$. This result indicates that the possible dislocation at the interface can be effectively prevented in our case, which has been confirmed by the smooth and clear interface in the HRTEM image. It is worth noting that in this configuration, five covalent bonds can be formed between CdS (Cd1 and S1*) and each $(\text{Sb}_4\text{X}_6)_n$ ribbon which possess two non-equivalent Sb atomic sites (Sb1, Sb2) and three non-equivalent S(e) atomic sites (S(e)1, S(e)2, S(e)3), namely Cd1-S(e)1, Cd1-S(e)2, Cd1-S(e)3, S1*-Sb1 and S1*-Sb2 (FIG. 15h). For quantitative structural analysis, we further carried out the full profile Rietveld refinement of $\text{Sb}_2(\text{S,Se})_3$ powder diffraction data (FIG. 17) and the detailed structural information is given in Table 3. The refined atomic occupancy indicates that 24% S has been replaced by Se in $\text{Sb}_2(\text{S,Se})_3$, which is in good agreement with the quantitative result of XPS analysis. In addition, the lattice constants as well as the cell volume of mixed-anion $\text{Sb}_2(\text{S,Se})_3$ increased compared to the pure Sb_2S_3 phase due to the partial replacement of S by the larger Se ions. We further measured the relevant atomic distances (labeled in FIG. 15f) and then calculated the corresponding atomic distance mismatches (Table 4, T. Kato *et al.*, *J. Cryst. Growth* **1998**, 183, 131-139). The significantly decreased lattice mismatch (absolute value) of L1, L3, L4 and L5 indicate that the current bonding configuration generates a small lattice mismatch between absorber and ETL. Furthermore, the enhanced rectangular symmetry in the mixed-anion $\text{Sb}_2(\text{S,Se})_3$ is believed to be beneficial for the bonding at the junction which can minimize potential defects attributed by interfacial distortion. As far as we know, this is the first time the hexagonal (100) CdS is confirmed to be a suitable substrate for the epitaxial growth of $\text{Sb}_2(\text{S,Se})_3$ along [001] direction.

Table 3. Rietveld refinement results for $\text{Sb}_2(\text{S,Se})_3$ powder.

Site	X	Y	Z	Atom	Occupancy	Elements ratio
Sb1	0.32560	0.03000	0.25000	Sb^{+3}	1	Se/(S+Se) = 24.3%
Sb2	0.03457	0.14839	0.75000	Sb^{+3}	1	
S1	0.87256	0.05286	0.25000	S^{-2}	0.8074	
				Se^{-2}	0.1926	
S2	0.43856	0.12772	0.75000	S^{-2}	0.7289	
				Se^{-2}	0.2711	

S3	0.19667	0.21191	0.25000	S ⁻²	0.7353	
				Se ⁻²	0.2647	
a = 11.398 Å, b = 11.537 Å, c = 3.889 Å, V = 511.53 Å ³ ; space group: Pbnm						

Table 4. Calculation of atomic distance mismatches between CdS and pure Sb₂S₃ and mixed Sb₂(S,Se)₃.

No.	Atomic distance (Å)			ADMs (%)	
	Sb ₂ S ₃	Sb ₂ (S,Se) ₃	CdS	Sb ₂ S ₃ //CdS	Sb ₂ (S,Se) ₃ //CdS
L1	2.58	2.56	2.53	1.98	1.19
L2	4.55	4.59	4.14	9.90	10.87
L3	3.90	4.12	4.14	-5.80	-0.48
L4	2.49	2.55	2.53	-1.58	0.79
L5	4.2	4.11	4.14	1.45	-0.72

5 Example 6. Optoelectronic properties of Sb₂(S,Se)₃ solar cell

TA measurements

TA measurements were conducted using a commercial HeliosTM setup from Ultrafast Systems, the pump and probe laser pulses were generated by frequency doubling the fundamental output (from of Coherent Legend, 150 fs, Ti-sapphire laser) and through white light generation with a sapphire plate, respectively. Current density-voltage (J-V) curves for solar cells were collected using Xe-based light source solar simulator (VS-0852 and KEITHLEY 2612A) to provide simulated AM 1.5G illumination which was calibrated against a standard Si reference cell. The active area of solar cell was defined by a 0.09 cm² shadow mask. The EQE measurement was performed by PVE300 (Bentham) IPCE Instrument and a Si reference cell was used for calibration.

For light intensity-dependent V_{OC} measurements, the J-V curves were collected at different light intensities using different neutral density filters. The light intensity-dependent V_{OC} measurement provides the information about the recombination process in the solar cell device. Under open-circuit conditions, the current is zero and all carriers recombine within the device according to the following equation:

$$V_{OC} = n \left(\frac{K_B T}{e} \right) \ln(I) + constant$$

Where n is the ideality factor, K_B is the Boltzmann constant, e is the elementary charge, T is the absolute temperature, and I is the light intensity. A plot of V_{OC} as a function of the logarithmic light intensity $\ln(I)$ is linearly fitted to evaluate the slope, which usually represents the recombination process caused by trap states in the device. If the ideality factor is close to 1, it means a bimolecular charge carrier recombination is the dominant recombination pathway in the device. On the contrary, the slope value close to 2 represents a trap-assisted charge recombination.

For temperature-dependent V_{OC} measurement, the J-V curves were collected by placing the samples in a continuous flow liquid nitrogen cryostat. Temperature-dependent V_{OC} measurements were performed in order to determine the activation energy (E_a) for the main recombination channel (S. S. Hegedus & W. N. Shafarman, *Prog. Photovoltaics Res. Appl.* **2004**, 12, 155-176). If a solar cell does not have a strong voltage dependent current collection or shunting, the relationship between the temperature and V_{OC} is given as follows:

$$V_{OC} = \frac{E_a}{q} - \frac{AkT}{q} \ln\left(\frac{J_{00}}{J_{SC}}\right)$$

where A is the diode ideality factor, kT/q is the thermal voltage, J_{00} is a temperature-dependent prefactor, q is the elementary charge and E_a is the activation energy of the recombination. E_a can be obtained through extrapolating to $T = 0$ K. Thus, if E_a equals to E_g (band gap) for the device, it indicates that the dominant recombination current occurs in the absorber layer while the gap of E_a with respect to E_g , namely $E_g - E_a$, reflects the strength of recombination caused by interfacial defects.

The TA spectroscopy (TAS) data was fitted with biexponential function:

$$y = A_1 e^{\frac{-t}{\tau_1}} + A_2 e^{\frac{-t}{\tau_2}} + C$$

Where A_1 and A_2 are prefactors, τ_1 and τ_2 are time constants, C is a constant and t is monitoring time. The average lifetime τ_{ave} is estimated from the fitting parameters according to the following equation:

$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

Where A_i and τ_i refer to A_1 and A_2 and τ_1 and τ_2 obtained from above fitting, respectively.

Results and discussion

As mentioned in the examples above, the performance of $Sb_2(S,Se)_3$ solar cells deteriorated at higher Cd concentration ($> 1\%$) even though the prepared absorber layer exhibited more

dominant (hk1) orientation. The reason was determined to be the parasitic absorption due to the formation of $\text{CdS}_x\text{Se}_{1-x}$ at the top of ETL. It was further confirmed by EQE analysis (FIG. 18a). It can be seen in FIG. 18a that the EQE for $\text{hk1-Sb}_2(\text{S,Se})_3$ device decreases in the short wavelength region (300–500 nm) with increasing Cd concentration from 0% to 4%. To quantify the current contribution from each part of the device, we calculated the integrated J_{SC} from EQE and then extracted the current difference between $\text{hk1-Sb}_2(\text{S,Se})_3$ and $\text{hk0-Sb}_2(\text{S,Se})_3$ device (denoted as $\Delta I_{\text{integrated}}(\text{Cell}_i\% - \text{Cell}_0\%)$) as the function of light wavelength. As shown in FIG. 18b, the wavelength region can be divided into three major regimes, namely, $\text{CdS}_x\text{Se}_{1-x}$ -affected area, $\text{Sb}_2(\text{S,Se})_3$ main absorption area, and unabsorbed area. For each line, the first cut-off point represents the band gap of $\text{CdS}_x\text{Se}_{1-x}$ which varied between 2.26–2.09 eV, depending on the Cd content while the second cut-off point represents the band gap of $\text{Sb}_2(\text{S,Se})_3$ having constant value of 1.55 eV. Taking the sample with 1% Cd as an example, the incorporation of Se led to the formation of $\text{CdS}_x\text{Se}_{1-x}$ with band gap value of 2.26 eV, resulting in a current loss of 0.76 mA/cm^2 caused by parasitic absorption. Fortunately, the current gain derived from the optimized crystal orientation of $\text{Sb}_2(\text{S,Se})_3$ was much more prominent in the visible light region, which not only compensated the current loss but also contributed to a substantial gain in PCE. However, the incorporation of higher Cd concentrations resulted in a more significant current reduction of more than 2.5 mA/cm^2 due to the increased Se content and thickness of $\text{CdS}_x\text{Se}_{1-x}$, leading to poor device performance.

The carrier recombination characteristics in $\text{Sb}_2(\text{S,Se})_3$ solar cells were studied by measuring the light intensity-dependent V_{OC} (FIG. 18c). The ideality factor was calculated to be 1.63, 1.47, 1.42, 1.40 and 1.39 for devices with increasing Cd content from 0% to 4%, respectively, which implies that the trap-assisted Shockley-Read-Hall (SRH) recombination was effectively suppressed after adding Cd. The underlying reasons should be ascribed to the regularly arranged grains in the (hk1)-oriented $\text{Sb}_2(\text{S,Se})_3$ film, in which the grain boundaries parallel to [001] direction are free of dangling bonds (R. Kondrotas, C. Chen & J. Tang, *Joule* **2018**, 2, 857-878), as well as the improved chemical bonding at the junction. To further figure out the dominant recombination processes in the device, temperature-dependent V_{OC} was studied (FIG. 18d). By linear fitting of the high temperature region and extrapolating to 0 K, the E_a of the main recombination channel can be extracted. It can be seen that the E_a for the recombination process in the device is closer to its band gap with increasing Cd concentration, suggesting that the interfacial recombination dominates the pristine $\text{hk0-Sb}_2(\text{S,Se})_3$. In other words, the possible interfacial trap states at the absorber/ETL interface mainly caused by the presence of uncoordinated ions has been passivated to some extent as the covalent bonding is formed between the ends of vertically oriented $(\text{Sb}_4\text{X}_6)_n$ ribbons and CdS substrate.

To evaluate the impact of crystal orientation on charge transfer kinetics in $\text{Sb}_2(\text{S,Se})_3$, TA characterization was carried out. The best performing $\text{Sb}_2(\text{S,Se})_3$ film prepared with 1% Cd was selected for comparison with the pristine one. The corresponding transient absorption spectra of $\text{hk1-Sb}_2(\text{S,Se})_3$ and $\text{hk0-Sb}_2(\text{S,Se})_3$ tracked at 10, 100, 1000 and 4000 ps after excitation are shown in FIG. 18e and 19, respectively. Both films show a typical combined photobleaching and photoinduced absorption feature in the range of 500–600 nm and 600–700 nm, respectively. It has been reported that the induced absorption peak in the visible region could be assigned to the formation of photogenerated hole localized on the crystal lattice of sulfur atoms (sulfide radical, denoted as S^- , J. A. Christians & P. V. Kamat, *ACS Nano* **2013**, 7, 7967-7974). The generated localized holes can decay through an electron-hole recombination process in the bulk of absorber. Thus, we monitored the signal at 650 nm to study the kinetics of trapped holes recombining with electron, which is a competitive process against electron extraction to ETL. As shown in FIG. 18f, the fast decay process indicates a shorter lifetime of sulfide radical. The obtained data were fitted with biexponential function and the results are presented in Table 5. The $\text{hk1-Sb}_2(\text{S,Se})_3$ sample exhibited a longer lifetime ($\tau_{\text{ave}} = 1.55$ ns) than that of $\text{hk0-Sb}_2(\text{S,Se})_3$ ($\tau_{\text{ave}} = 1.26$ ns), which indicates the faster processes of electron transport in the bulk absorber and extraction by ETL for $\text{hk1-Sb}_2(\text{S,Se})_3$ sample.

Table 5. Fitting results of TAS.

Sample	A_1	$\tau_1(\text{ps})$	A_2	$\tau_2(\text{ns})$	$\tau_{\text{ave}}(\text{ns})$
hk0-Sb₂(S,Se)₃	0.12	70 ± 5	0.52	1.28 ± 0.01	1.26 ± 0.01
hk1-Sb₂(S,Se)₃	0.18	130 ± 13	0.34	1.61 ± 0.02	1.55 ± 0.02

FIG. 20a displays the J-V curve of the highest efficiency device based on $\text{hk1-Sb}_2(\text{S,Se})_3$ absorber measured under AM1.5G illumination. The cell exhibited a V_{OC} of 0.604 V, a J_{SC} of 21.62 mA/cm^2 , and a FF of 70.49%, delivering a PCE of 9.21% ($\text{PCE} = V_{\text{OC}} \cdot J_{\text{SC}} \cdot \text{FF} / 100$), which is among the highest reported for planar $\text{Sb}_2(\text{S,Se})_3$ solar cells. It is believed that the (hk1)-oriented $\text{Sb}_2(\text{S,Se})_3$ guarantees efficient charge transport along the vertically oriented $(\text{Sb}_4\text{X}_6)_n$ ribbons, corresponding to a lower recombination rate in the bulk of $\text{Sb}_2(\text{S,Se})_3$ (T. Kumari *et al.*, *Energy Environ. Sci.* **2017**, 10, 258-265), and thus better J_{SC} and V_{OC} for the device. In addition, it is worth highlighting that the high fill factor (FF) of the device can be attributed to the passivated interface of $\text{Sb}_2(\text{S,Se})_3/\text{CdS}$ heterojunction, enabling an efficient charge collection by ETL. The corresponding EQE curve is shown in FIG. 20b. The maximum value reaches up to 90% at 570 nm, and the integrated current density was calculated to be 21.78

mA/cm², which is consistent with the measured J_{SC} value. FIG. 20c shows the typical cross-sectional SEM image of the complete device. The optimized thickness of $Sb_2(S,Se)_3$ absorber layer was determined to be around 400 nm.

- 5 As mentioned above, the introduction of Cd during the hydrothermal process facilitates the vertical growth of $(Sb_4X_6)_n$ ribbons and the highest efficiency device was obtained at 1% Cd concentration. Although the [hk1] orientation in $Sb_2(S,Se)_3$ film continues to strengthen at higher Cd concentration, as noted from the XRD analysis, the device performance deteriorates instead. This was attributed to the parasitic absorption of CdSe having a lower band gap,
- 10 poisoning the CdS ETL.

Claims

1. A method of forming a film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$, comprising the steps of:
 - (a) placing a substrate, comprising:
 - a first layer formed from SnO_2 ; and
 - a second layer on top of the first layer, the second layer providing a surface for $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ growth, the second layer formed from CdS in hexagonal form, where the surface is substantially formed from a (100) facet of the hexagonal CdS,
 against a wall of a vessel, such that the substrate is positioned at an angle relative to a base of the vessel;
 - (b) immersing the substrate in an aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ and conducting a hydrothermal reaction for a period of time at a temperature of from 100 to 150 °C to grow the film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ on the second layer of the substrate, wherein the precursor solution further comprises a cadmium (II) salt in an amount to provide a molar percentage of Cd relative to the amount of Sb ($n_{\text{Cd}}/n_{\text{Sb}}$) of from 1 to 5%; and x is from 0 to 1.
2. The method according to Claim 1, wherein the product of step (b) of Claim 1 is annealed at a temperature of from 250 to 400 °C, such as from 300 to 350 °C, such as about 335 °C for a period of from 5 minutes to 1 hour, such as from 10 to 40 minutes, such as from 15 to 30 minutes, such as about 20 minutes.
3. The method according to Claim 1 or Claim 2, wherein:
 - (ai) the period of time in step (b) of Claim 1 is from 1 to 10 hours, such as from 2 to 4 hours, such as about 3.5 hours; and/or
 - (aii) the temperature in step (b) of Claim 1 is from 120 to 150 °C, such as from 125 to 130 °C.
4. The method according to any one of the preceding claims, wherein the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ comprises $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 3\text{H}_2\text{O}$ and one or both of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and $\text{SeC}(\text{NH}_3)_2$, optionally wherein the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ comprises $\text{K}_2\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, but not $\text{SeC}(\text{NH}_3)_2$.
5. The method according to any one of the preceding claims, wherein the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ comprises a molar ratio of Sb:S of from 1:2 to 1:5 (e.g. about 1:4.8) and a molar ratio of Sb:Se of from 1:0 to 1:0.3 (e.g. about 1:0.24).

6. The method according to any one of the preceding claims, wherein the aqueous precursor solution of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ comprises a cadmium (II) salt in an amount ($n_{\text{Cd}}/n_{\text{Sb}}$) of from 1 to 4%, such as from 2 to 3.5%, such as from 2.5 to 3.25%, such as about 3%.

7. The method according to any one of the preceding claims, wherein the angle is from 20 to 60°, such as about 40°.

8. The method according to any one of the preceding claims, wherein the substrate is formed by the steps of:

(bi) providing a precursor substrate comprising a first layer of SnO_2 and a second layer formed from CdS; and

(bii) coating a C_1 to C_3 alcohol solution of an oversaturated cadmium (II) salt for a first period of time on the precursor substrate to provide an intermediate substrate, which is then annealed for a second period of time at a temperature of from 350 to 500 °C, optionally wherein the C_1 to C_3 alcohol is methanol.

9. The method according to Claim 8, wherein:

(ci) the second period of time is from 5 to 20 minutes, such as about 10 minutes; and/or

(cii) the temperature is from 400-420 °C, such as 415 °C.

10. The method according to Claim 8 or Claim 9, wherein the precursor substrate is formed by the steps of:

(di) providing a SnO_2 substrate comprising a surface formed by SnO_2 ; and

(dii) immersing the SnO_2 substrate in a CdS precursor solution at a temperature of from 45 to 100 °C for a period of time to form the precursor substrate, optionally wherein the SnO_2 substrate further comprises an electrode layer, more optionally wherein the electrode layer is formed from ITO glass or, more particularly, FTO glass.

11. The method according to Claim 10, wherein:

(ei) the period of time is from 10 to 20 minutes, such as about 15 minutes; and/or

(eii) the temperature is from 60 to 80 °C, such as about 65 °C.

12. The method according to Claim 8 or Claim 9, wherein the SnO_2 substrate is formed by the steps of:

(fi) providing a blank substrate material having a surface; and

(fii) spin-coating the surface of the blank substrate with a solution comprising SnO_2 nanoparticles to provide the SnO_2 substrate.

13. The method according to Claim 12, wherein:

(gi) the SnO_2 nanoparticles have a diameter of from 1 to 20 nm, such as from 3 to 4 nm; and/or

(gii) the SnO_2 substrate obtained in step (fii) of Claim 12 is subjected to annealing for a period of time at an elevated temperature, optionally wherein the period of time is from 10 minutes to 1 hour, such as about 30 minutes, and the elevated temperature is from 100 to 200 °C, such as about 150 °C; and/or

(giii) the spin-coating in step (fii) of Claim 12 was conducted at a speed of from 1000 to 3500 rpm for a period of time, optionally wherein the speed is about 2500 rpm and/or the period of time is about 30 seconds.

14. The method according to any one of the preceding claims, wherein:

(aai) the hexagonal CdS has (100) and (101) facets and the surface of the second layer is formed from the (100) and (101) facets of the hexagonal CdS, where the ratio of intensity of the (100) facet to the (101) facet in the X-ray diffraction pattern is greater than or equal to 1.3; and/or

(aaii) the cadmium (II) salt is CdSO_4 or has the formula CdX_2 , where each X is a halide or NO_3 , optionally wherein X is I, Br or, more particularly, Cl;

(aa iii) the relationship of the second layer and the film of $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ to each other is $(001)_d \parallel [001]_d \parallel (100)_s [210]_s$.

15. The method according to any one of the preceding claims, wherein a hole transport layer is placed on the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ and an electrode is placed on the hole transport layer, optionally wherein the hole transport layer is spiro-OMeTAD and the electrode is gold and/or silver (e.g. a layer of gold and/or silver that is from 30 to 100 nm thick, such as 60 nm thick).

16. A light absorbing device comprising:

a first electron transport layer formed of SnO_2 ;

a CdS layer on the first electron transport layer as a second electron transport layer;

a $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer on the CdS layer as a light absorbing layer; and

a hole transport layer on the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer, wherein

the CdS layer is formed from CdS in hexagonal form, where the surface is substantially formed from a (100) facet of the hexagonal CdS and the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer is formed from a plurality of parallel $(\text{Sb}_4\text{X}_6)_n$ ribbons that extend from the CdS layer in a [001] direction.

17. The light absorbing device according to Claim 16, wherein the relationship of the CdS layer and the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer to each other is $(001)_d \parallel [001]_d \parallel (100)_s [210]_s$.

18. The light absorbing device according to Claim 16 or Claim 17, wherein the first electron transport layer formed of SnO_2 has a first surface and a second surface, where the first surface is attached to a transparent electrode material and the second surface is attached to the CdS layer.

19. The light absorbing device according to Claim 18, wherein the transparent electrode material is selected from ITO glass or, more particularly, FTO glass.

20. The light absorbing device according to any one of Claims 16 to 19, wherein the hexagonal CdS has (100) and (101) facets and the surface of the second electron transport layer is formed from the (100) and (101) facets of the hexagonal CdS, where the ratio of intensity of the (100) facet to the (101) facet in the X-ray diffraction pattern is greater than or equal to 1.3.

21. The light absorbing device according to any one of Claims 16 to 20, wherein:

(hi) the hole transport layer has a first surface attached to the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer and a second surface attached to an electrode material; and/or

(hii) the hole transport layer is an organic semiconductor or an inorganic semiconductor with p-type conductivity, optionally wherein the hole transport layer is selected from one or more of the group consisting of P3HT, PbS, MnS, CuSCN, and, more particularly, spiro-OMeTAD.

22. The light absorbing device according to Claim 21, wherein the electrode material is a layer of gold and/or silver (e.g. a layer of gold and/or silver that is from 30 to 100 nm thick, such as 60 nm thick).

23. The light absorbing device according to any one of Claims 16 to 22, wherein the $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ layer is formed by a plurality of $(\text{Sb}_4\text{X}_6)_n$ ribbons oriented in (hk1) planes, optionally wherein the $(\text{Sb}_4\text{X}_6)_n$ ribbons display one or more (hk1) planes selected from the (101), (111), (211) and (221).

24. The light absorbing device according to Claim 23, wherein one or more of the following apply:

the (101) plane has a texture coefficient of greater than or equal to 1.80;

the (111) plane has a texture coefficient of greater than or equal to 1.20;
the (211) plane has a texture coefficient of greater than or equal to 1.10; and
the (221) plane has a texture coefficient of greater than or equal to 1.10.

25. The light absorbing device according to any one of Claims 16 to 24, wherein the light absorbing device displays a power conversion efficiency of from 9.0 to 10%, such as about 9.24%.