

Review

# Advances on $\text{Sb}_2\text{Se}_3$ Solar Cells Fabricated by Physical Vapor Deposition Techniques

Roberto Jakomin <sup>1</sup>, Stefano Rampino <sup>2,\*</sup> , Giulia Spaggiari <sup>2,3</sup>  and Francesco Pattini <sup>2</sup>

<sup>1</sup> Campus Duque de Caxias, Universidade Federal do Rio de Janeiro, Rio de Janeiro 25240-005, Brazil; robertojakomin@xerem.ufrj.br

<sup>2</sup> Consiglio Nazionale delle Ricerche, IMEM Institute, 43124 Parma, Italy; giulia.spaggiari1@unipr.it (G.S.); francesco.pattini@cnr.it (F.P.)

<sup>3</sup> Department of Mathematical, Physical and Computer Sciences, University of Parma, Parco Area delle Scienze 7/a (Campus), 43124 Parma, Italy

\* Correspondence: stefano.rampino@cnr.it

**Abstract:**  $\text{Sb}_2\text{Se}_3$ , as an earth-abundant and low-toxic material, has emerged as one of the most interesting absorbers for clean renewable power generation technologies. Due to its optical properties, especially bandgap and absorption coefficient, the number of papers on  $\text{Sb}_2\text{Se}_3$ -based solar cells has been constantly increasing in the last ten years, and its power conversion efficiency has raised from 1% in 2014 to 10.57% in 2022. In this review, different  $\text{Sb}_2\text{Se}_3$  solar cells' fabrication technologies based on physical vapor deposition are described and correlated to the texture coefficient (ribbon orientation). Moreover, recent research works of the most promising solar cell configurations with different electron-transporting layers and hole-transporting layers are analyzed with a special emphasis on photovoltaic performances. Furthermore, different  $\text{Sb}_2\text{Se}_3$  doping techniques are discussed. All these aspects are considered as new strategies to overcome the  $\text{Sb}_2\text{Se}_3$  solar cell's actual limitations.

**Keywords:**  $\text{Sb}_2\text{Se}_3$ ; solar cells; physical vapor deposition; chalcogenides



**Citation:** Jakomin, R.; Rampino, S.; Spaggiari, G.; Pattini, F. Advances on  $\text{Sb}_2\text{Se}_3$  Solar Cells Fabricated by Physical Vapor Deposition Techniques. *Solar* **2023**, *3*, 566–595. <https://doi.org/10.3390/solar3040031>

Academic Editor: Dongsheng Li

Received: 3 August 2023

Revised: 18 September 2023

Accepted: 28 September 2023

Published: 12 October 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Thin-film solar cells are the most promising alternative to crystalline silicon solar cells because they use less material, are less expensive, and can be integrated into flexible devices. Chalcogenide thin-film solar cells, especially those based on CdTe and Cu(In,Ga)Se<sub>2</sub>, are the most dominant in the thin-film photovoltaic market due to their good stability and efficiency (22.1% for CdTe and 23.35% for CIGS) [1]. Perovskite solar cells have also achieved high efficiencies up to 23.7% in recent years, but they are still not reliable enough for mass production.

Silicon (Si)-based solar cells are the dominant technology in the photovoltaic (PV) market. They have a high power-to-cost ratio due to their high efficiency (up to 26.7%) and the fact that silicon is abundant on Earth. However, the production of single-crystal silicon wafers is energy-intensive, and silicon must be more than 100  $\mu\text{m}$  thick to absorb enough sunlight [2]. Chalcogenide materials, on the other hand, have a high optical absorption coefficient, which allows them to be made into lighter and more flexible panels, and they also have lower material and energy production costs.

Among chalcogenides, antimony selenide ( $\text{Sb}_2\text{Se}_3$ ) has attracted attention as a potential absorber material for thin-film solar cells due to its excellent optical (very high absorption coefficient  $>10^5 \text{ cm}^{-1}$ ) and electrical (p-type conductivity between  $10^{-7} \text{ S/cm}$  and  $4.6 \times 10^2 \text{ S/cm}$ ) properties. It is also a binary semiconductor with a low melting point of 608 °C.

Furthermore, the scarcity of indium and the toxicity of cadmium have led to increased interest in this type of material, which is made from abundant elements such as Se, Sb, and S that are not considered to be highly toxic or carcinogenic.

Another interesting feature of  $\text{Sb}_2\text{Se}_3$  is that there is still a lot of room for improvement in its research. In fact, with its 1.2 eV band gap [3], the Shockley–Queisser theory predicts a theoretical power conversion efficiency (PCE) of 31.7% [4]. The highest experimental efficiency achieved so far is 10.57% [5]. In comparison, silicon solar cells have been developed for over 70 years and have reached their efficiency limit. In contrast,  $\text{Sb}_2\text{Se}_3$  solar cells have rapidly increased their efficiency from 1% to 10.57% in less than 10 years.

$\text{Sb}_2\text{Se}_3$  forms one-dimensional ribbons along the c-axis through Sb–Se covalent bonds [6]. The ribbons are stacked together in the perpendicular directions by weaker van der Waals forces [7].

The quasi-one-dimensional structure of  $\text{Sb}_2\text{Se}_3$  induces strong anisotropic properties, especially for electrical conductivity. The carrier mobility of the ribbons oriented along the (001) growth direction is higher than along other directions.

This is because surfaces parallel to the (001) direction, such as (110) and (120) surfaces, have no dangling bonds and consequently lead to reduced nonradiative recombination losses [6].

In particular, the hole mobility along the ribbons is high ( $45 \text{ cm}^2/\text{Vs}$  at 300 K), while the carrier transport perpendicular to the covalent bond directions is much smaller because it is associated with a hopping conduction mechanism [8].

In order to maximize the efficiency of  $\text{Sb}_2\text{Se}_3$  solar cells, it is important to align the ribbons closer to the growth direction (perpendicular to the substrate), such as the (211) and (221) crystal orientations. It is also important to minimize the grain orientation along the (hk0) directions.

The low experimental efficiency of  $\text{Sb}_2\text{Se}_3$  solar cells is mainly due to the following factors:

- Short carrier lifetime: The carrier lifetime is the average time that a charge carrier (electron or hole) can exist before it recombines with another carrier. The short carrier lifetime in  $\text{Sb}_2\text{Se}_3$  is due to the high density of defects, such as Se vacancies and  $\text{Sb}_{\text{Se}}/\text{Se}_{\text{Sb}}$  antisite defects [9].
- Low hole density: The hole density is the number of holes per unit volume in a semiconductor material. The low hole density in intrinsic  $\text{Sb}_2\text{Se}_3$  is another factor that limits the efficiency of the solar cells [2].
- Lack of suitable hole and electron transport layer materials: The hole transport layer (HTL) and electron transport layer (ETL) are the materials that transport the holes and electrons, respectively, to the respective electrodes of the solar cell. The lack of suitable HTL and ETL materials is also a challenge for the development of high-efficiency  $\text{Sb}_2\text{Se}_3$  solar cells [10].

In order to reduce interface/surface defects, strategies such as defect passivation have been explored. Defect passivation is the process of covering the defects with a material that will prevent them from recombining with charge carriers. This can be done by selenizing the surface of the  $\text{Sb}_2\text{Se}_3$  or by covering it with a passivating layer [11].

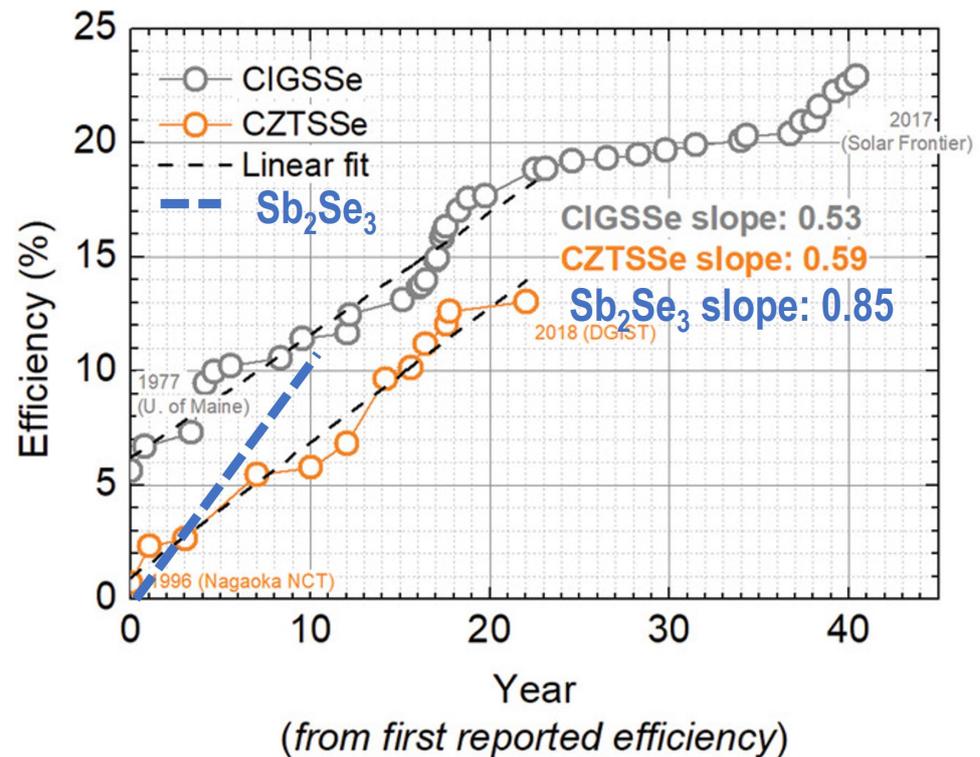
The band alignment between the electron transport layer (ETL) and hole transport layer (HTL) and  $\text{Sb}_2\text{Se}_3$  is not ideal, which causes an inefficient extraction and transport of photocarriers at the interface with the absorber.

The commonly used ETLs include CdS,  $\text{TiO}_2$ , ZnO, and  $\text{SnO}_2$ . The HTLs that have been reported in the literature are organic, such as spiro-OMeTAD, P3HT, PCDTBT, and CZ-TA, or inorganic, such as  $\text{NiO}_x$ , CuSCN, and  $\text{CuSbSe}_2$  [12].

In the past few years, several studies have been published on the deposition of  $\text{Sb}_2\text{Se}_3$  thin films for solar cells. One common method is the spin-coating deposition on mesoporous oxides in dye-sensitized solar cells (DSSC) structures [13]. This method is simple and scalable, but it can be difficult to control the thickness and uniformity of the film.

Another common method is to deposit  $\text{Sb}_2\text{Se}_3$  from the vapor phase. This can be done using a variety of technique: these methods can produce high-quality films with a good control over thickness and uniformity.

Recently, close-spaced sublimation (CSS) and injection vapor deposition (IVD) have demonstrated power conversion efficiencies (PCE) of 9.2% (in 2019) and 10.12% (in 2022), respectively. The record of 10.57% (in 2022) was achieved using additive-assisted chemical bath deposition (CBD) [5]. Although the number of laboratories involved in  $\text{Sb}_2\text{Se}_3$  research is still small, the improvements in cell efficiency have been even faster than those achieved in CIGS and CZTS technologies in their first 10 years of research (Figure 1) [14].



**Figure 1.** Record efficiencies versus time for  $\text{Sb}_2\text{Se}_3$ -, CIGSSe-, and CZTSSe-based solar cells. Year 0 is 1977 for CIGSSe [15], 1997 for kesterites [16], 2013 for  $\text{Sb}_2\text{Se}_3$ . Adapted with permission from [14] Copyright © 2019, John Wiley and Sons.

Although significant progress has been made in increasing the efficiency of  $\text{Sb}_2\text{Se}_3$  solar cells, many challenges remain, such as surface/interface recombination, effective doping, and optimal HTL/absorber/ETL band alignment.

The photocarrier mobility is strongly dependent on the grain orientation, so controlling the ribbon orientation is one of the most important goals for  $\text{Sb}_2\text{Se}_3$  absorbers in photovoltaic applications. The texture coefficient is hence a fundamental parameter for evaluating the potential of different deposition methods. However, although many studies have reported their texture coefficients, the relative values are rarely calculated, making it difficult to directly compare the obtained absorbers.

This paper reviews recent advances in  $\text{Sb}_2\text{Se}_3$  solar cells fabricated in planar configuration using physical deposition techniques (PDT). The different relative texture coefficients (TCs) have been extrapolated from the available literature data, which allows for the comparison of ribbon alignment for different deposition methods and structures, and their correlation with the main solar cell performance. The different ETL/absorber/HTL solar cell architectures are then discussed, especially considering their band alignment strategies for enhancing photovoltaic performance. Finally, the different doping strategies for  $\text{Sb}_2\text{Se}_3$ -based absorbers are summarized, evaluating the achieved carrier transport properties and the reported solar cell efficiencies.

The paper is divided into four sections. Section 2 describes the different physical deposition techniques (PDTs) used to fabricate  $\text{Sb}_2\text{Se}_3$  solar cells. Section 3.1 correlates

the PDTs and cell configurations with the ribbon orientation. Section 3.2 discusses the different HTL/ETL, interfacial engineering, and band alignment strategies that have been reported in the literature. Section 3.3 shows the different doping strategies for  $\text{Sb}_2\text{Se}_3$ -based absorbers. Finally, the paper summarizes the challenges and outlines future perspectives for the development of  $\text{Sb}_2\text{Se}_3$  photovoltaics, with a special emphasis on increasing conversion efficiency.

The authors believe that comparing and discussing the recently published works, with a special focus on ribbon orientation, ETL/HTL, and doping issues, can support future research to limit interface and defect recombination, especially affecting the open-circuit voltage ( $V_{oc}$ ), and improve photocarrier extraction in  $\text{Sb}_2\text{Se}_3$  solar cells.

## 2. Physical Vapor Deposition Techniques for Planar-Type Structure $\text{Sb}_2\text{Se}_3$ Solar Cells

Planar-configuration  $\text{Sb}_2\text{Se}_3$  solar cells have generally achieved better performance than mesoporous structure cells, especially due to a higher open circuit voltage,  $V_{oc}$ . This is because in planar cells, defects introduced by chemical solvents, such as pinholes, are avoided, thus achieving a higher crystallinity.

Planar-type structures can be classified into two configurations: substrate and superstrate.

In the substrate architecture, the device configuration generally includes (starting from the top):

- A transparent electrode layer or metal grid (Al or Au)
- A window layer (for example undoped ZnO)
- An ETL (for example CdS)
- An  $\text{Sb}_2\text{Se}_3$  absorber layer
- An HTL
- A metallic or conductive oxide back-contact
- A glass substrate.

The substrate architecture comes from the CIGS technology, which exhibits main advantages, such as the versatility in choosing different substrates and the possibility of fabricating tandem, bifacial, and eventually flexible cells [10].

Superstrate solar cells are a type of solar cell where the absorber layer is deposited on top of the other layers. This is in contrast to a substrate solar cell, where the absorber layer is deposited on the bottom.

In superstrate solar cells, the device configuration is generally formed by [10]:

- A metal contact
- An HTL (for example Spiro-MeOTAD, P3HT, NiOx)
- An  $\text{Sb}_2\text{Se}_3$  absorber layer
- An ETL (for example  $\text{TiO}_2$  or CdS)
- A transparent conductive oxide
- Glass (substrate).

Superstrate configuration cells take origin from the CdTe technology and generally exhibit the highest PCE values. This is because the interfaces in superstrate cells are less prone to defects.

In this section, we briefly describe the most interesting PDT for the growth of  $\text{Sb}_2\text{Se}_3$  absorber layers:

- Magnetron sputtering;
- Close-spaced sublimation (CSS);
- Rapid thermal evaporation (RTE);
- Vapor transport deposition (VTD);
- Injected vapor deposition (IVT);
- Pulsed laser deposition (PLD);
- Pulsed electron deposition (PED).

### 2.1. Magnetron Sputtering

In radiofrequency magnetron sputtering (RF-MS), argon ions are accelerated by a radiofrequency electric field to hit a target. This removes material from the target, which is then deposited on a substrate that can be heated (Figure 2a).

Sb<sub>2</sub>Se<sub>3</sub> is obtained by sputtering material from a high-purity, stoichiometric Sb<sub>2</sub>Se<sub>3</sub> target at a working pressure of 0.5–1.5 Pa [17–19]. The chamber is filled with pure argon gas (99.99%). The RF power is fixed at 30–40 W.

In an alternative method proposed by C. Ma et al. [20], Sb<sub>2</sub>Se<sub>3</sub> films can be deposited through co-sputtering of Sb<sub>2</sub>Se<sub>3</sub> and Se targets. The pressure is maintained at 0.5 Pa. The RF power on the Sb<sub>2</sub>Se<sub>3</sub> target is fixed at 30 W, while the RF power on the Se target is changed during the processing from 0 W to 15 W.

In another method, a thin film of metallic Sb is deposited by RF magnetron sputtering from a high-purity and dense Sb sputtering target. Highly crystalline Sb<sub>2</sub>Se<sub>3</sub> thin films are obtained by a post-growth post-selenization heat treatment to induce the in situ combination reaction (from Se highly pure powder) [21].

### 2.2. Close-Spaced Sublimation

In CSS, the source material and the substrate are close to each other, at 1–5 mm, at the extremities of a graphite box. Deposition occurs in a vacuum atmosphere (or in certain cases in gases such as H<sub>2</sub>, argon, nitrogen). The solid-state source (powder) and the substrate are heated at different temperatures: the former is heated to a temperature that favors sublimation (Figure 2b) while the latter is kept at a lower temperature to promote the condensation in thin-film form. The method offers the advantage of high deposition rates, and it is widely used to deposit semiconductor materials such as CdTe [22]. More recently, this method was also used to fabricate Sb<sub>2</sub>Se<sub>3</sub>-based solar cells [23,24]. Thanks to the low melting point of Sb<sub>2</sub>Se<sub>3</sub> (608 °C) and the high saturated vapor pressure (around 100 Pa at 550 °C), CSS is a low-energy-consumption technique for Sb<sub>2</sub>Se<sub>3</sub> growth, and it is more likely to form (hkℓ)-oriented grains with ℓ ≠ 0, especially at certain substrate temperatures. An optimal ribbon orientation allowed the CSS-grown Sb<sub>2</sub>Se<sub>3</sub> solar cell to reach a high 9.2% efficiency [25].

### 2.3. Rapid Thermal Evaporation

RTE [6,26,27] is a vacuum process similar to CSS, but in this case, the material melts and evaporates from the liquid phase, not from the solid phase as in a sublimation process.

The deposition method is carried out in a tube furnace, generally maintained at a low vacuum by a mechanical pump (0.5–1 Pa) [6,25]. The distance between source and substrate is within 10 mm. In this process, a rapid increase in temperature and fast deposition are possible, so growth times are generally limited to a few seconds.

For example, H. Guo et al. [26] set a deposition time of 40 s, a preheating temperature of 310 °C for 20 min and the deposition temperature of 570 °C. A PCE of 7% was obtained for a simple Au/Sb<sub>2</sub>Se<sub>3</sub>/CdS/ITO/glass superstrate solar cell.

### 2.4. Vapor Transport Deposition

In the VTD method, both the substrate temperature and source-to-substrate distance can be adjusted. A carrier gas is saturated with a vapor from a subliming source (high-purity powder) and conducted towards the substrate at lower temperature, where the film growth occurs (Figure 2c). Sb<sub>2</sub>Se<sub>3</sub> absorber-based solar cells fabricated through VTD exhibited an efficiency of 7.6% in a Au/Sb<sub>2</sub>Se<sub>3</sub>/CdS/ITO/glass solar cell structure [28].

### 2.5. Injected Vapor Deposition

IVD has been recently developed by Z. Duan et al. [29]. It is a promising technique for the fabrication of Sb<sub>2</sub>Se<sub>3</sub> solar cells because it has been demonstrated to achieve one of the highest efficiencies (more than 10%) measured so far.

In an IVD system, the precursor of the  $\text{Sb}_2\text{Se}_3$  powder is placed into a roller, which is heated at  $490^\circ\text{C}$ . Argon gas is injected from one side of the roller and forms an  $\text{Sb}_2\text{Se}_3$  vapor which reaches the heated substrate on the opposite side (Figure 2d). In IVD, the injection gas flow is the most crucial parameter affecting the quality of the material and thus the solar cell performance.

### 2.6. Pulsed Laser Deposition

In PLD, usually in a vacuum chamber, the plume is formed by a high-power pulsed laser beam that hits a target of the material that must be deposited (Figure 2e). The deposition occurs when the material condensates on the substrate, facing the target, which is maintained at an adjustable temperature. An  $\text{Sb}_2\text{Se}_3$  absorber deposited at  $500^\circ\text{C}$  by PLD reached an efficiency of 4.77% [30,31].

### 2.7. Pulsed Electron Deposition

PED is a physical deposition technique where a pulsed electron beam is accelerated by a high voltage to ablate a solid material target. The interaction between electrons and target material forms a plasma plume through the fast sublimation of the target which condensates on the surface of a substrate, placed at a few centimeters in front of it (Figure 2f). The nonequilibrium fast solid-vapor transition induces a transfer of material with the same stoichiometry as the target to the substrate.  $\text{Sb}_2\text{Se}_3$  layers have been grown in an argon atmosphere of 0.3 Pa, setting a discharge voltage of 16 kV, a pulse rate of 9 Hz, with the substrate temperature maintained between 200 and  $400^\circ\text{C}$ . The optimized solar cell based on an  $\text{Sb}_2\text{Se}_3$  absorber grown by PED (with the substrate structure AZO/ZnO/CdS/ $\text{Sb}_2\text{Se}_3$ /Mo/glass) showed an efficiency of 2.1% [32,33].

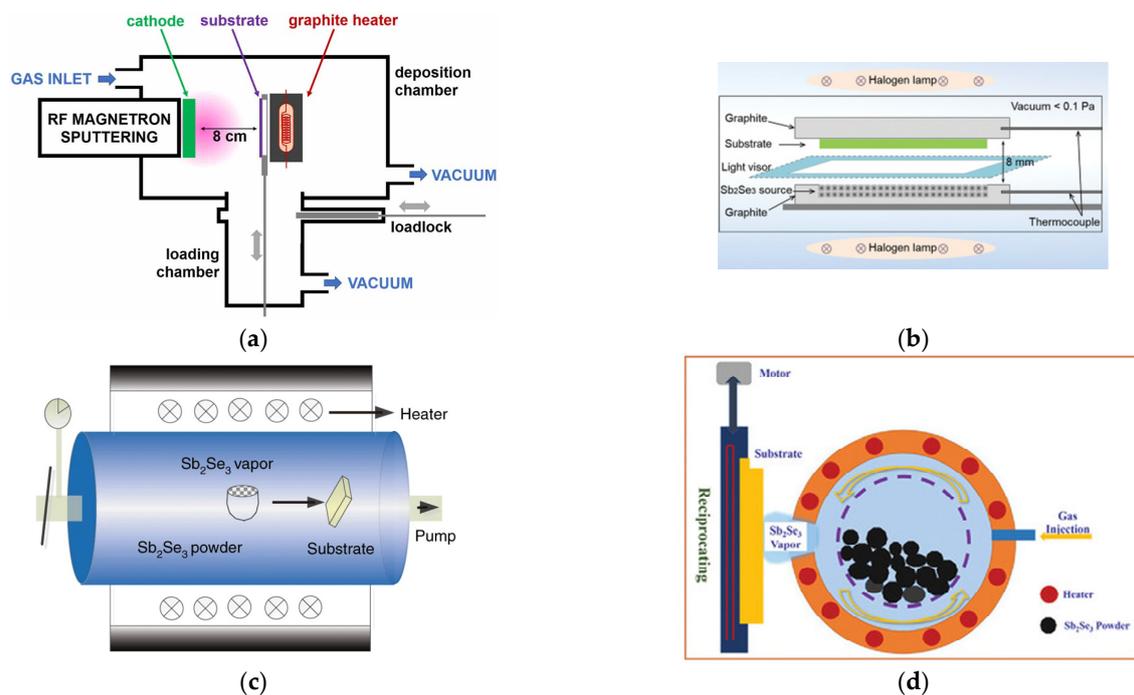
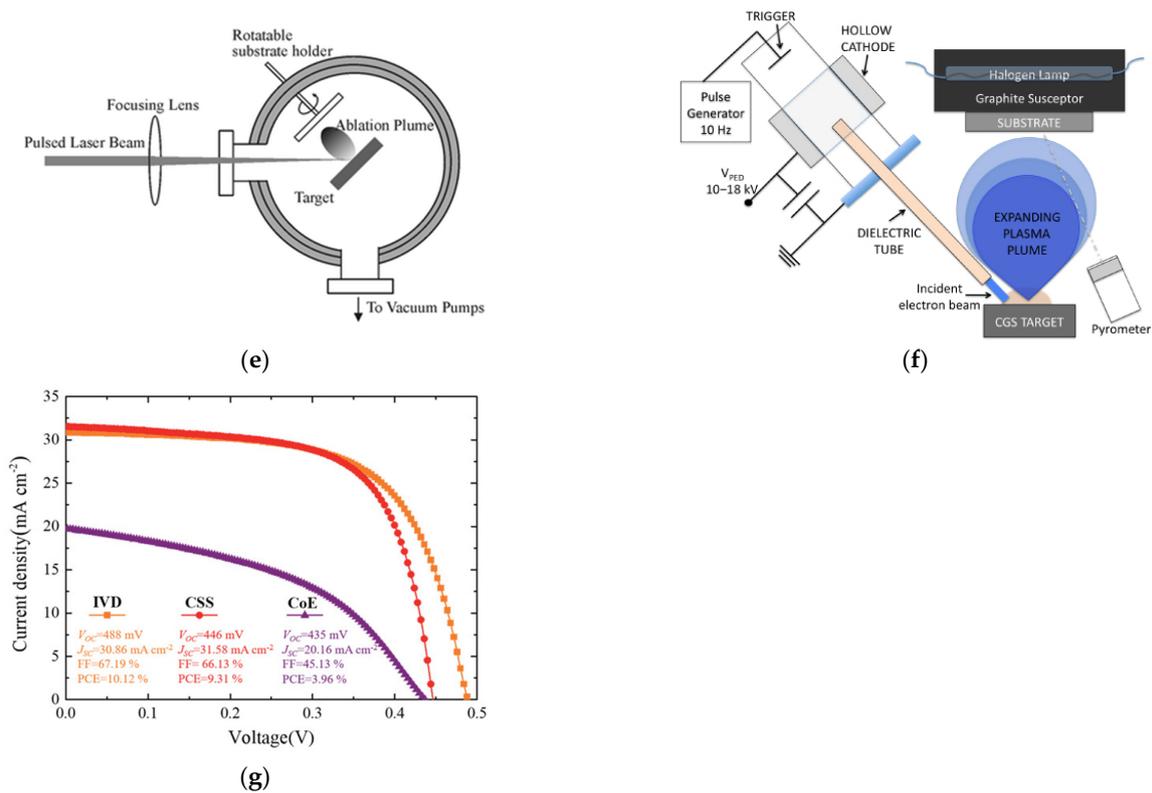


Figure 2. Cont.



**Figure 2.** Schematized setups of different PVD systems: (a) RF-MS. Reproduced with permission from [19]. © 2021 IOP Publishing. (b) CSS. Reproduced from [34]. © 2020 K. Shen et al. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) VTD. Reproduced from [28]. © 2018, X. Wen et al., <http://creativecommons.org/licenses/by/4.0/> (accessed on 15 September 2023). (d) IVD. Reproduced with permission from [29]. © 2022 John Wiley & Sons. (e) PLD. Reproduced with permission from [31]. © The Royal Society of Chemistry 2004. (f) PED. Reproduced with permission from [33]. © 2013 IOP Publishing. (g) Current density–voltage (J–V) curves of the IVD-, CSS-, and CoE (co-evaporated)-Sb<sub>2</sub>Se<sub>3</sub> solar cells. Reproduced with permission from [29]. © 2022 John Wiley & Sons.

### 3. The Main Challenges for Sb<sub>2</sub>Se<sub>3</sub>—Based Solar Cells (1D-Ribbon Alignment, HTL/ETL, Interfacial Engineering and Band Alignment, Doping)

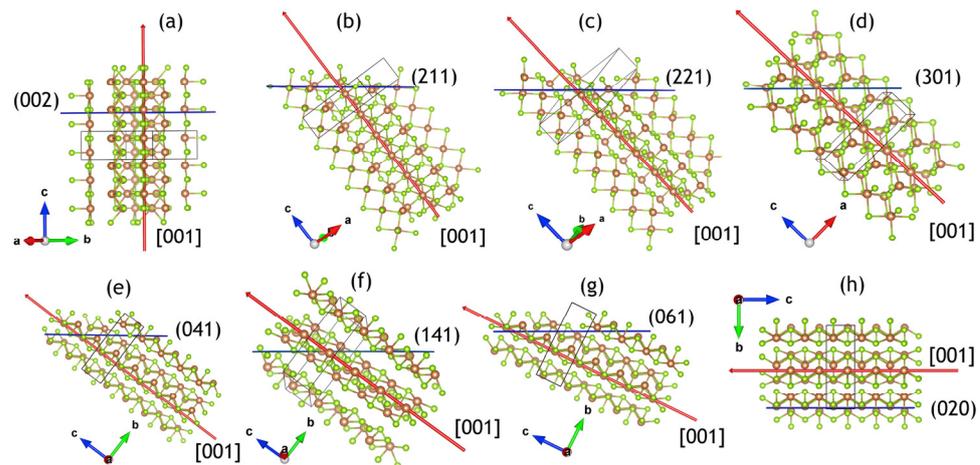
#### 3.1. One-Dimensional-Ribbon Alignment

As discussed in Section 1, Sb<sub>2</sub>Se<sub>3</sub> is characterized by a one-dimensional crystal structure, a ribbonlike morphology, which determines strong anisotropic electrical conduction and optical properties (Figure 3). Crystal orientation control is crucial for the deposition of high-quality Sb<sub>2</sub>Se<sub>3</sub> films. Sb<sub>2</sub>Se<sub>3</sub> has a one-dimensional crystal structure, which gives it strong anisotropic electrical conduction and optical properties. Researchers are working hard to obtain vertically (or quasi-vertically) oriented Sb<sub>2</sub>Se<sub>3</sub> ribbons, i.e., parallel to the growth direction. Several factors influence the crystal orientation of Sb<sub>2</sub>Se<sub>3</sub>, including the deposition technique, the substrate, the postdeposition treatments, and the use of pre-growth seeding methods. It is known that the best transport properties for PV applications can be achieved if the *c* axis of the crystal structure is normal to the surface (0,0,*l*), while the worst conditions are obtained when the *c* axis lies on the surface (*h*,*k*,0). It is difficult to compare different results in the literature in terms of grain orientations and their correlation to photovoltaic performance. This is because the relative texture coefficient, TC (*hk**l*), is rarely reported. TC (*hk**l*) is the ratio between the measured (*hk**l*) peak intensity and the intensity of the same peak for a reference, randomly oriented powder, weighted as a

percentage of the summation of the same value for all chosen peaks [35]. On the other hand, not all the reflections are always considered. TC ( $hk\ell$ ) is given by the following equation:

$$TC(hk\ell) = \frac{I(hk\ell)}{\sum_n I_0(hk\ell)} \times 100 (\%)$$

where  $I_0(hk\ell)$  is the relative intensity of the reflection with ( $hk\ell$ ) Miller indices reported in the JCPDS card, and  $I(hk\ell)$  is the net intensity measured by the experimental XRD patterns after the background subtraction.



**Figure 3.** Graphical representations of the  $(Sb_4Se_6)_n$  ribbons inclination (red arrow,  $Sb^{3+}$  = brown dots,  $Se^{2+}$  = green dots) corresponding to the (001) direction with respect to the growing surface (blue line) under different out-of-plane grain orientations ( $hk\ell$ ): (a) (002), (b) (211), (c) (221), (d) (301), (e) (041), (f) (141), (g) (061) and (h) (020), respectively.. Reproduced with permission from [32], © 2020 Elsevier B.V.

In Table 1, we list several works where relative TC ( $hk\ell$ ) (for the summation of reflections  $h = 0, k = 0$ , and  $\ell \neq 0$ ) for  $Sb_2Se_3$  films have been extrapolated from the reported graphs and at least around 10 reflections have been shown. The  $\Sigma$  TC ( $\ell \neq 0$ ) parameter represents the percentage of vertically oriented ribbons. Vertically oriented ribbons do not lie on the substrate surface, and thus, they contribute to the electrical conduction.

**Table 1.** Extrapolated  $\Sigma$  TC ( $\ell \neq 0$ ) values and reported PCE and  $J_{sc}$  for different deposition methods and underlying layers.

Deposition Method	Substrate/Underlayer	$\Sigma$ TC ( $hk\ell$ ) $\ell \neq 0$	Observations	PCE	$J_{sc}$ ( $mA/cm^2$ )	Reference
CSS	TiO <sub>2</sub> /FTO/glass	86%	With seeding layer	3.8%	21.1	[36]
CSS	TiO <sub>2</sub> /FTO/glass	65.4%	W/o seeding layer	1.6%	24.9	[36]
CSS	CdS/FTO/glass	89.5%	CdCl <sub>2</sub> treatment	6.23%	27.36	[36]
CSS	CdS/FTO/glass	88.1%	//	4.27%	21.74	[21]
CSS	CdS/FTO/glass	97.5%	CdS by CCS	2.82%	19.5	[37]
CSS	TiO <sub>2</sub> /FTO/glass	~100%	Seeding layer	5.28%	24.6	[37]
CSS	TiO <sub>2</sub> /CdS/FTO/glass	~100%	//	2.07%	15.6	[37]
CSS	SnO <sub>2</sub> /FTO/glass	58.3%	CdCl <sub>2</sub> treatment	//	//	[38]
CSS	SnO <sub>2</sub> /FTO/glass	5.4%	No treatments	//	//	[38]

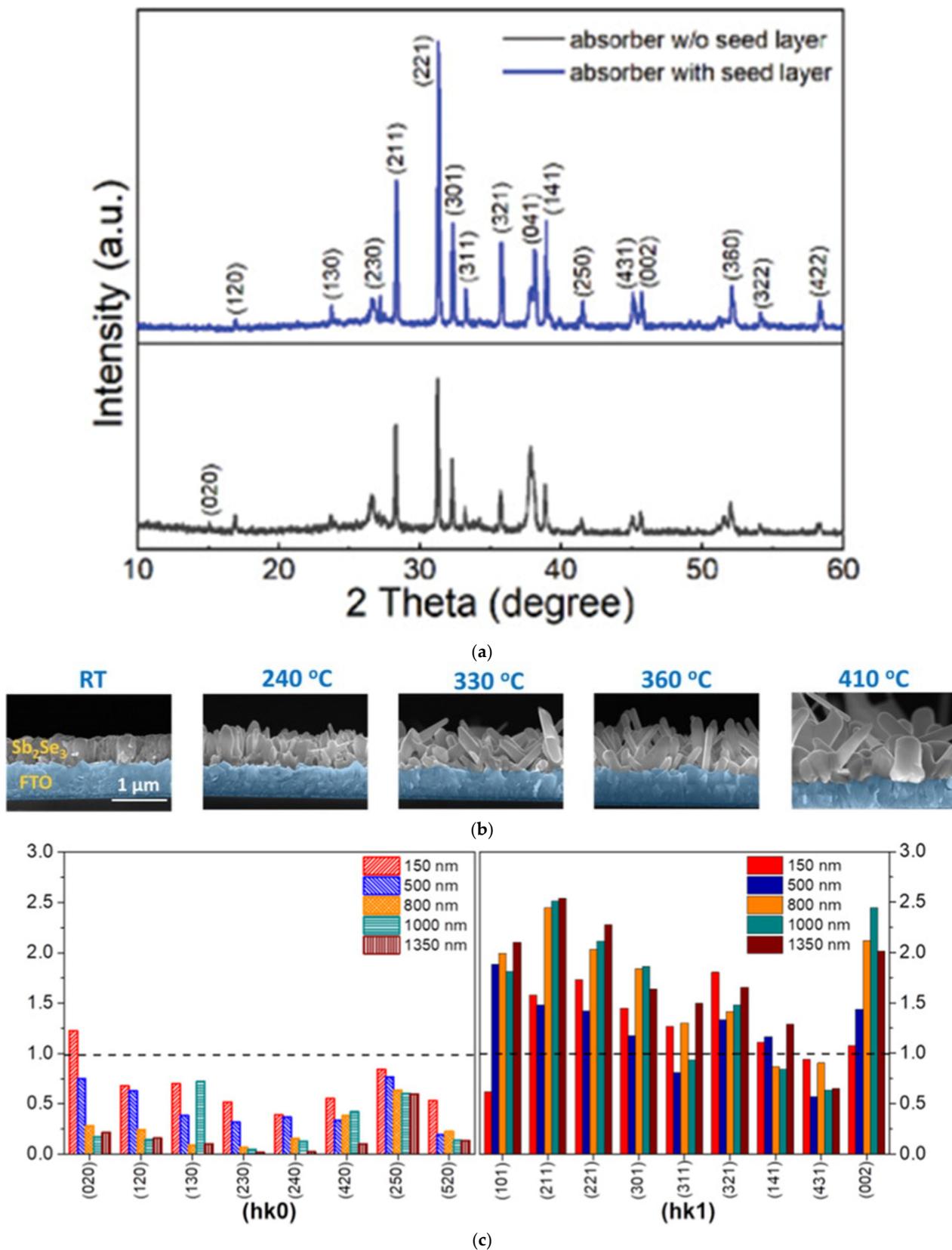
Table 1. Cont.

Deposition Method	Substrate/Underlayer	$\Sigma$ TC (hk $\ell$ ) $\ell \neq 0$	Observations	PCE	$J_{sc}$ (mA/cm <sup>2</sup> )	Reference
CSS	FTO/glass	92.2%	330 °C	9%	29.8	[39]
VTD	SnO <sub>2</sub> /ITO/glass	91.4%	//	2.7%	19.3	[40]
VTD	TiO <sub>2</sub> /ITO/glass	30.9%	//	2%	23.6	[40]
VTD	SnO <sub>2</sub> /TiO <sub>2</sub> /ITO/glass	~100%	//	4.8%	25.6	[40]
VTD	CdS/TiO <sub>2</sub> /ITO/glass	64.7%	CdS-VTD	4.91%	28.6	[41]
VTD	CdS/TiO <sub>2</sub> /ITO/glass	50.1%	CdS-CBD	4.24%	28.3	[41]
RTE	CdS/FTO/glass	90.4%	w/o KOH treatment	4.8%	28.13	[26]
RTE	CdS/FTO/glass	92.1%	with KOH treatment	7.16%	//	[26]
RF sputtering	CdS/FTO/glass	71.3%	Annealing at 460 °C	6.06%	25.91	[42]
RF sputtering	FTO/glass	60%	//	1.28%	24.83	[19]
RF sputtering	CdS/FTO/glass	91%	//	2.36%	27.06	[19]
RF sputtering	Mo	30%	//	0.24%	5.11	[19]
PED	FTO/glass	60.2%	//	2.1%	20.3	[32]
PED	CdS/FTO/glass	38.4%	//	//	//	[32]
PED	Mo	0.6%	//	//	0.3	[32]
Thermal co-evaporation	Mo	73.5%	Substrate T = 300 °C	2.67–4.51%	19.51	[43]

In general, the CSS technique and the more recent IVD allow for more vertically oriented ribbons because the material is directly sublimated from the solid, and deposition occurs at high growth rates. In the paper by Krautmann et al., Sb<sub>2</sub>Se<sub>3</sub> is deposited on TiO<sub>2</sub> with a seeding layer procedure: a 60 nm seed layer (SL) at 300 °C and then 1.8 micron at 450 °C [36]; the SL growth at low temperature is fundamental to create ribbonlike seeds on which subsequent columnar structures can grow. Vertical ribbons (002) planes show a TC of 1.2 for Sb<sub>2</sub>Se<sub>3</sub> with an SL and 0.2 without an SL. The extrapolated  $\Sigma$  TC (hk $\ell$ )  $\ell \neq 0$  was 86% with an SL and 65.4% without an SL, respectively. As a consequence, solar cells with a higher TC show an efficiency of 3.8% and solar cells without an SL an efficiency of 1.6%, and an increase in the short circuit current density,  $J_{sc}$ , from 21.1 to 24.9 mA/cm<sup>2</sup> when the SL is used. In [44], the authors showed that the first grown 750 nm Sb<sub>2</sub>Se<sub>3</sub> layer on CdS/FTO was compact, and ribbonlike structures started to grow at a higher growth time on the compact layer; (211), (221), (301), and (311) orientations prevailed when the entire film thickness was between 1.3 and 2.7  $\mu$ m. A maximum PCE of 6.23% and a  $J_{sc}$  of 28.53 mA/cm<sup>2</sup> was obtained for a 2.1  $\mu$ m thick Sb<sub>2</sub>Se<sub>3</sub> with a  $\Sigma$  TC (hk $\ell$ )  $\ell \neq 0$  of 89.5%. The use of CuInSe<sub>2</sub> sensitizer quantum dots (QDs) to passivate defects of the Sb<sub>2</sub>Se<sub>3</sub> nanorod structure allowed a 7.6% PCE.

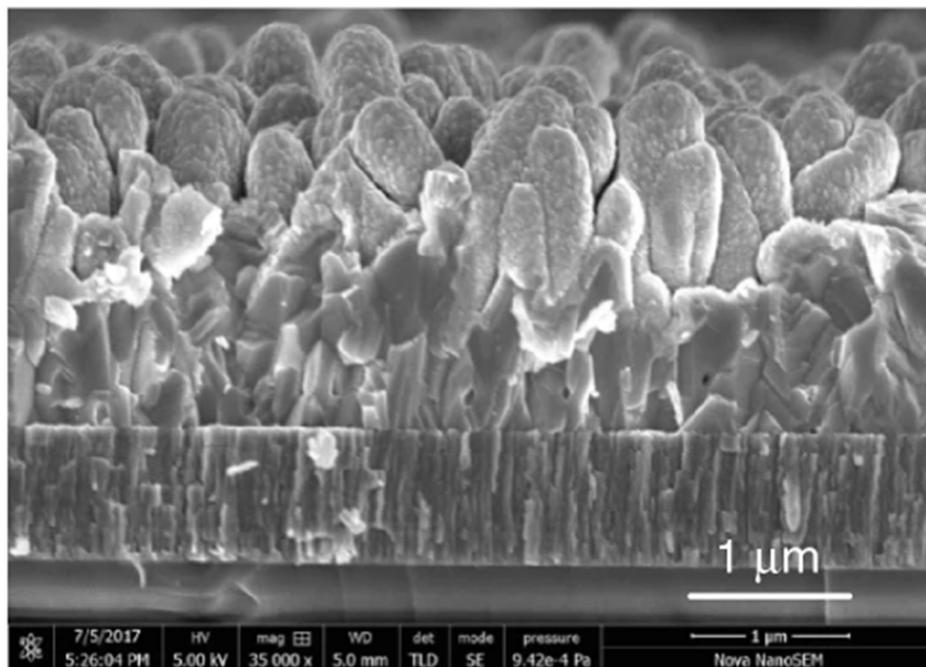
In [34], the Sb<sub>2</sub>Se<sub>3</sub> SL deposited by a CSS process on CdS was 10 nm thick and subsequently an Sb<sub>2</sub>Se<sub>3</sub> absorber layer of 500 nm was deposited on the SL. In that case, the SL was grown by setting the source and substrate temperatures at 310 °C for 120 s, raising the source to 510 °C in 60 s (setting the substrate temperature at around 330 °C) and then keeping the source temperature at 510 °C for 10 s. The main absorber layer deposition was performed after a natural cooling to 270° of the substrate. In that case, the film grown after the seed layer showed a more (221) preferred orientation (Figure 4a), a PCE of 7.45%, and a  $J_{sc}$  of almost 30 mA/cm<sup>2</sup> was achieved for Au/t-Se/Sb<sub>2</sub>Se<sub>3</sub>/CdS/FTO cells.

L. Guo et al. [23] emphasized the importance of growth temperature and time during CSS growth. In fact, they observed that (211) oriented grains dominated in films thicker than 0.6  $\mu$ m, and (hk0) orientations were strongly limited at substrate temperatures lower than 300 °C.  $\Sigma$  TC (hk $\ell$ )  $\ell \neq 0$  was 88.1% and graphite/Sb<sub>2</sub>Se<sub>3</sub>/CdS/FTO/glass samples reached a  $J_{sc}$  of 21.74 mA/cm<sup>2</sup> and a 4.27% PCE, in that case.

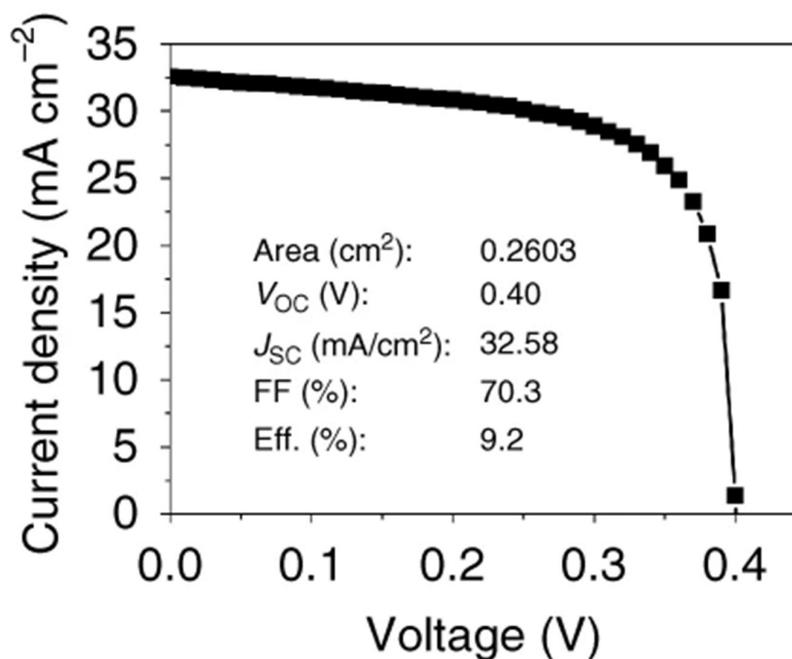


**Figure 4.** (a) XRD spectra of the  $Sb_2Se_3$  films deposited by a seed layer-assisted successive CSS process and single CSS process. Reproduced from [34]. © 2020 K. Shen et al. Published by WILEY-VCH Verlag GmbH & Co. KgaA, Weinheim. (b) Cross-section images of  $Sb_2Se_3$  absorber at different temperatures. (c) TC of  $Sb_2Se_3$  absorber with different thicknesses. Reproduced with permission from [39]. © 2022 John Wiley & Sons.

Z. Li et al. [25] studied the evolution from a thin-layer film to a nanorod array for  $\text{Sb}_2\text{Se}_3$  on Mo coated glass substrates deposited by CSS (Figure 5). As in the previous case, deposition time is important for 1D growth: they observed that the  $\text{Sb}_2\text{Se}_3$  structure varied from a compact thin film to an aligned nanorod array with increasing growth durations (from 60 to 180 s). The nanorod alignment promoted a  $J_{\text{SC}}$  of  $32.58 \text{ mA/cm}^2$  leading to a PCE of 9.2%.



(a)



(b)

**Figure 5.** (a) Cross-sectional SEM image of the completed CdS/ $\text{Sb}_2\text{Se}_3$  solar cells; (b) illuminated J-V curve of the same cell. Reproduced from [25]. Copyright 2019 Z. Li et al., <http://creativecommons.org/licenses/by/4.0/> (accessed on 15 September 2023).

C. Guo et al. [45] studied the incorporation of a Ag element into  $\text{Sb}_2\text{Se}_3$  obtaining quasi-vertical 1D ribbons at 280 °C, which vanished at 420 °C, where the (120) preferential orientation prevailed. Solar cells of AZO/ZnO/ $(\text{Sb}_2\text{Se}_3)_x(\text{AgSbSe}_2)_{1-x}$ /MoSe<sub>2</sub>/Mo/glass achieved a  $J_{\text{sc}}$  of 25.29 mA/cm<sup>2</sup> and a 7.8% of PCE when the substrate temperature was set at 320 °C.

In [39], another CSS growth was adopted to obtain  $\text{Sb}_2\text{Se}_3$ , and the authors found that the formation of the  $\text{Sb}_2\text{Se}_3$  crystal was not strongly dependent on the substrate temperature. However, (hk0) planes, parallel to the substrate, decreased for growth temperature >240 °C (up to 410 °C), while most of the TCs for the (hk1) planes, oblique or perpendicular to the substrate, increased with the growth temperature between 240 °C and 410 °C.  $\Sigma \text{TC}(\text{hk}\ell)$   $\ell \neq 0$  was 92.2% in this case and AZO/i-ZnO/CdS/ $\text{Sb}_2\text{Se}_3$ /FTO/glass solar cells with a 1350 nm (Figure 4b,c) thick  $\text{Sb}_2\text{Se}_3$  layer demonstrated a  $J_{\text{sc}}$  of 29.5 mA/cm<sup>2</sup> and a conversion efficiency of 9.0%.

P. Fan et al. [46] investigated  $\text{Sb}_2\text{Se}_3$  obtained by CSS followed by a selenization process on a Mo/SLG (soda-lime glass) substrate. They studied different temperature ramp for the source during sublimation: from 260 or 290 °C for 2 min to 510 or 520 °C for 2 min. In the selenization process, the Se powder and the as-grown  $\text{Sb}_2\text{Se}_3$  thin film, placed at a distance of 23 cm, were simultaneously heated at 400 and 420 °C for 15 min, respectively. It was found that the (hk0) grain orientation decreased by increasing the temperature from 260 to 290 °C, while the TC values of the (hk1) and (hk2) increased with the temperature, finding an optimum substrate temperature to stimulate the (hk1) orientation for 290 °C. Moreover, the subsequent post-selenization treatment led to large grain sizes with the preferred (hk1) orientation. In these optimized conditions, the authors obtained a high 509 meV  $V_{\text{oc}}$ , with a  $J_{\text{sc}}$  of 21.15 mA/cm<sup>2</sup> reaching a PCE of 4.86% with a Ag/ITO/CdS/ $\text{Sb}_2\text{Se}_3$ /Mo solar cell.

N. Spalatu et al. [37] grew  $\text{Sb}_2\text{Se}_3$  absorbers by CSS, finding a preferred orientation of grains along the (211) and (221) crystal directions for depositions at 450 °C. For temperatures rising from 300 to 450 °C, the TC values of the (301) and (151) planes increased systematically, and the TC of the (020) and (120) planes decreased. A maximum efficiency of 2.8% was demonstrated for Au/ $\text{Sb}_2\text{Se}_3$ /CdS/FTO/glass solar cells with an  $\text{Sb}_2\text{Se}_3$  absorber obtained at 450 °C, with a  $\Sigma \text{TC}(\text{hk}\ell)$   $\ell \neq 0$  of 97.5%. Better performance of PCE around 5.3% was achieved with a superstrate configuration  $\text{TiO}_2$ / $\text{Sb}_2\text{Se}_3$  cell where an  $\text{Sb}_2\text{Se}_3$  seed layer was implemented at the interface and where  $\Sigma \text{TC}(\text{hk}\ell)$   $\ell \neq 0$  was around 100%. The SL consisted of a ~60 nm thick  $\text{Sb}_2\text{Se}_3$  layer deposited at a low T of 300 °C by CSS at the interface between buffer and absorber layers, and it was fundamental in that work to enhance the efficiency from 1.66% ( $J_{\text{sc}}$  of 19.8 mA/cm<sup>2</sup>) to 5.28% ( $J_{\text{sc}}$  of 24.6 mA/cm<sup>2</sup>).

A. Amin et al. [47] fabricated  $\text{Sb}_2\text{Se}_3$  by CSS on a nanorods (NR)-CdS/nanoparticles (NP)-CdS buffer layer. The nanorod CdS (NR-CdS) buffer layer was synthesized by a hydrothermal method while the NP CdS films were prepared by the CBD method. The authors observed that the NR-CdS and NR-CdS/NP-CdS buffer layers favored the (211) orientation of the  $\text{Sb}_2\text{Se}_3$  ribbons and the reduction in the (120) orientation. Thanks to the control of the nanoribbon orientation, the  $\text{Sb}_2\text{Se}_3$  solar cell reached a PCE of 7.16%.

S. Pasini et al. [48] showed the Influence of the window layer on the  $\text{Sb}_2\text{Se}_3$  ribbon orientation for a superstrate configuration solar cell. A preferential growth of the CSS-grown  $\text{Sb}_2\text{Se}_3$  along the (001) direction on window layers containing zinc, with a TC for the (002) reflection reaching the maximum value of 27% and a 4.5% efficiency with a ZnCdS ( $\text{Zn}_{0.15}\text{Cd}_{0.85}\text{S}$ ) window layer (with a solar cell structure of Pt/ $\text{Sb}_2\text{Te}_2$ / $\text{Sb}_2\text{Se}_3$ /ZnCdS/ZnO/ITO/glass) was observed.

In the case of the VTD process, X. Wen et al. [28] obtained  $\text{Sb}_2\text{Se}_3$  grown on CdS/ITO, studying an evaporation temperature between 480 and 510 °C, reached with a ramp rate of 20 °C/min followed by a plateau of 2 min. When the source temperature was at 510 °C, corresponding to a substrate temperature of 390 °C, the film exhibited the highest crystallinity and XRD intensity of the preferred (221) orientation. Thus, the Au/ $\text{Sb}_2\text{Se}_3$ /CdS/ITO/glass solar cells showed a  $J_{\text{sc}}$  of 29.9 mA/cm<sup>2</sup> leading to a 7.6% PCE.

J. Kim et al. studied  $\text{Sb}_2\text{Se}_3$  deposition by VTD [49], by co-evaporation from  $\text{Sb}_2\text{Se}_3$  and Se sources. The chamber pressure was 3 mTorr, with a source temperature of 560 °C and a substrate temperature of 300 °C. The authors observed that Se flux control was very important for the film characteristics. In fact, an extra supply of Se contributed to suppress undesirable vacancies  $V_{\text{Se}}$ , while an excessive Se overpressure inhibited the (221) orientation growth, which was detrimental to electrical transport properties. A superstrate configured solar cell ( $\text{Au}/\text{Sb}_2\text{Se}_3/\text{CdS}/\text{ITO}/\text{glass}$ ) showed a PCE of 5.2% in optimized conditions. S. Dong et al. [50] proposed a modified VTD method, in a double-temperature-zone furnace, to obtain  $\text{Sb}_2\text{Se}_3$  with Se in excess. A  $\text{CdS}/\text{ITO}/\text{glass}$  substrate was placed on the graphite bracket at the extremity of the furnace, the Se powder was kept at a higher temperature than the melting point (>270 °C) to ensure a stable supply of Se was placed at the other end of the tubular furnace above its thermal baffle, and two quartz crucibles containing  $\text{Sb}_2\text{Se}_3$  powder were put in the center of the two temperature zones. The authors showed that (221) orientations increased with the Se flux; thus, with the Se excess, and a  $\text{Au}/\text{Sb}_2\text{Se}_3/\text{CdS}/\text{ITO}/\text{glass}$  structure, the PCE was improved from 5.1% to 6.7%, and  $J_{\text{sc}}$  from 27.7 to 30.5  $\text{mA}/\text{cm}^2$  with the absorber grown in Se-rich conditions.

W. Wang et al. [40] implemented VTD-grown  $\text{Sb}_2\text{Se}_3$  on  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2/\text{TiO}_2$ ,  $\text{CdS}$ , and  $\text{SnO}_2/\text{TiO}_2/\text{CdS}$  ETL. They observed that  $\text{SnO}_2$  or/and  $\text{SnO}_2/\text{TiO}_2$  ETL underlayers favored the formation of (041), (141), and (061) ( $\Sigma$  TC ( $hkl$ )  $l \neq 0$  of 91.4% and almost 100%, respectively) more than in the case of  $\text{TiO}_2$  ( $\Sigma$  TC ( $hkl$ )  $l \neq 0$  of 30.9%). Since the  $\text{CdS}$  interlayer was also important to reduce the band offset, the  $\text{Sb}_2\text{Se}_3/\text{CdS}/\text{TiO}_2/\text{SnO}_2/\text{ITO}/\text{glass}$  solar cell achieved a  $J_{\text{sc}}$  of 29.9  $\text{mA}/\text{cm}^2$  and PCE of 7%.

In [41], the authors fabricated a  $\text{CdS}$  layer by VTD with a better conductivity and higher crystallinity than with CBD. They observed that the  $\text{CdS}$ -buffer layer induced the growth of  $\text{Sb}_2\text{Se}_3$  with an (hk1) orientation, such that the extrapolated  $\Sigma$  TC ( $l \neq 0$ ) was around 64.7% for  $\text{Sb}_2\text{Se}_3$  grown on a  $\text{CdS}$  layer deposited by VTD and 50.1% for the one grown on  $\text{CdS}$  obtained by CBD. Thus, they obtained a 4.91% PCE for the  $\text{CdS}$ -VTD-based device, and 4.24% for the  $\text{CdS}$ -CBD.

In [51], a  $\text{CdS}$  ETL was also modified with  $\text{Al}_2\text{O}_3$  grown by atomic layer deposition as the interface layer at the  $\text{CdS}/\text{Sb}_2\text{Se}_3$  interface. The  $\text{Sb}_2\text{Se}_3$  absorber layer was deposited on  $\text{Al}_2\text{O}_3$  by VTD in a dual-temperature-zone tube furnace, showing a strong increase in TCs of (hk1) and decrease in (hk0) in the presence of  $\text{Al}_2\text{O}_3$ . Therefore, the authors obtained a PCE of 6.25% for a carbon/ $\text{Sb}_2\text{Se}_3/\text{Al}_2\text{O}_3/\text{CdS}/\text{FTO}/\text{glass}$  solar cell configuration.

V. Kumar et al. [52] compared thermally evaporated  $\text{Sb}_2\text{Se}_3$  subjected to three different processes: just annealing, simultaneous evaporation of  $\text{Sb}_2\text{Se}_3/\text{Se}$  during the absorber growth, and post-deposition selenization. They observed that the  $\text{Sb}_2\text{Se}_3$  layer grew spontaneously with predominant (221) and (321) orientations. Then, post-deposition annealing and co-selenization reduced (321) in favor of the (141) orientation, while in the case of the postselenization, the (221) orientation had a stronger intensity, and the (041) orientation was also present.

Surface treatments can also induce columnar-mode growth as observed from H. Guo et al. [53]. In that case, the RTE method was used to fabricate  $\text{Sb}_2\text{Se}_3$  in a  $\text{Au}/\text{Al}_2\text{O}_3/\text{P}^+-\text{Sb}_2\text{Se}_3/\text{P}-\text{Sb}_2\text{Se}_3/\text{CdS}/\text{FTO}/\text{glass}$  structure in which the  $\text{CdS}$  layer was submitted to an oxygen plasma treatment before the  $\text{Sb}_2\text{Se}_3$  growth. The effect was a decrease in the  $\text{CdS}$  grain size, a reduction in film roughness, and the introduction of oxygen atoms. The authors argued that the increase in the O content in the  $\text{CdS}$  surface stimulated a higher crystallinity and the columnar growth of  $\text{Sb}_2\text{Se}_3$ , thus an increase in  $J_{\text{sc}}$  from 22.03  $\text{mA}/\text{cm}^2$  to 26.26  $\text{mA}/\text{cm}^2$  and PCE from 2.48 to 5.1% was observed for solar cells without or with plasma treatment, respectively. Moreover, a subsequent  $\text{Al}_2\text{O}_3$  layer, deposited by atomic layer deposition (ALD) method, increased by two orders of magnitude the hole concentration for  $\text{Sb}_2\text{Se}_3$  film, leading to a PCE of 6.7%.

In [54], an  $\text{Sb}_2\text{Se}_3$  nanorod-array was prepared on the Mo substrate at a low temperature by RTE. The authors showed the importance of the SL growth temperature; the SL was performed at 360 °C while 480 °C was the  $\text{Sb}_2\text{Se}_3$  growth temperature, resulting in a

preferred orientation in the (211) direction and a minimum TC value for the (230) diffraction peak. In this manner, they showed an efficiency of 6.3% in a ZnO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/Mo/SLG solar cell structure.

X. Wen et al. [55] fabricated a highly (001)-oriented Sb<sub>2</sub>Se<sub>3</sub> film on a flexible mica where Sb was thermally evaporated, followed by a selenization process into a horizontal quartz tube furnace at 410 °C. In this way, Ag/ITO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/Mo/mica grid flexible solar cells obtained an efficiency of 8.42%, a J<sub>sc</sub> of 31.30 mA/cm<sup>2</sup>, and a V<sub>oc</sub> of 0.47 V.

A KOH treatment also induces preferential grain orientation, as observed in [26], where the TC ratio between the (221) and (211) peaks was higher in the Sb<sub>2</sub>Se<sub>3</sub> film exposed to 0.07 M KOH than that in the not-treated films, showing a  $\Sigma$  TC (hkℓ) ℓ ≠ 0 higher than 90%. This concentration was found to be optimal, leading to a 7.16% efficiency and a J<sub>sc</sub> of 30.68 mA/cm<sup>2</sup> in a Au/Sb<sub>2</sub>Se<sub>3</sub>/CdS/FTO/glass solar cell. At the same time, the KOH solution (0.07 M) treatment played a doping role, through a diffusion of K species; in fact, the hole concentration of the Sb<sub>2</sub>Se<sub>3</sub> film increased from 10<sup>13</sup> cm<sup>-3</sup> to 10<sup>15</sup> cm<sup>-3</sup>; for higher concentrations (0.15 M), the carrier density decreased, probably due to corrosion.

J. Zhou et al. showed how the SnO<sub>2</sub> underlayer deposition and treatment could influence the Sb<sub>2</sub>Se<sub>3</sub> orientation [38]. In that case, Sb<sub>2</sub>Se<sub>3</sub> grown by CSS on treated SnO<sub>2</sub>, with a CdCl<sub>2</sub> methanol solution, showed a high preferential (211) 1D orientation,  $\Sigma$  TC (hkℓ) ℓ ≠ 0 was 58.3% versus 5.4% for the not-treated surface. The authors claimed that this effect was due to the formation of Cd-[Sb<sub>4</sub>S<sub>6</sub>]<sub>n</sub> ribbon covalent bonds.

Now, considering the sputtering method, G-X. Liang et al. [17] obtained Sb<sub>2</sub>Se<sub>3</sub> nanorods with the preferred crystallographic orientation of (221) at a substrate temperature of 375 °C, and a deposition pressure and power of 0.5 Pa and 30 W, respectively. The same conditions at room temperature led to amorphous Sb<sub>2</sub>Se<sub>3</sub> films. AZO/ZnO/CdS/Sb<sub>2</sub>Se<sub>3</sub> nanorods/Mo solar cells exhibited a 2.1% PCE.

R. Tang et al. [42] reported on a sputtered Sb<sub>2</sub>Se<sub>3</sub> cell obtained by a two-step process (growth of amorphous Sb<sub>2</sub>Se<sub>3</sub> by RF-MS followed by a selenization process). The selenization step was performed in an evacuated tubular furnace successively filled with pure Ar at a pressure of 5 × 10<sup>4</sup> Pa. The highly pure Se powder was heated at 400 °C while Sb<sub>2</sub>Se<sub>3</sub> was kept at a lower temperature. Temperature is critical during selenization so that the growth of vertical rods is favored when selenization is performed up to 420 °C, then (hk0)-oriented grains start to increase. For the best T,  $\Sigma$  TC (hkℓ) ℓ ≠ 0 was 71.3%, J<sub>sc</sub> was 25.91 mA/cm<sup>2</sup>, and the efficiency of a Ag/ITO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/Mo reached 6.06%. For S. Rijal et al. [56], in Sb<sub>2</sub>Se<sub>3</sub> grown by CSS on Mo-coated glass, higher temperatures in selenization enhanced crystallinity, as the average grain size increased with the selenization temperature. The highest TC values of the (211) and (221) planes for the film annealed at 425 °C indicated a preferred Sb<sub>2</sub>Se<sub>3</sub> ribbon orientation at this selenization temperature. As a consequence, J<sub>sc</sub> increased from 18.6 mA/cm<sup>2</sup> to 22.9 mA/cm<sup>2</sup>, and the PCE from 1.85% to 6.43%.

C. Yuan et al. obtained [57] an Sb<sub>2</sub>Se<sub>3</sub> film by a two-step method: DC-MS of metallic Sb followed by selenization through a rapid thermal process (RTE). The selenization process was conducted with temperatures between 320 and 440 °C for 5 min, under vacuum conditions. The thin films selenized with temperatures below 400 °C exhibited a preferred orientation along the (211) plane and (221) plane, while the morphology quality decreased for higher annealing temperatures with the appearance of holes and a lower carrier mobility. The best achieved efficiency for an Al/Al:ZnO/ZnO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/Mo solar cell was 3.47%, and J<sub>sc</sub> = 16 mA/cm<sup>2</sup> for selenization performed at 400 °C.

G. Spaggiari et al. [19] observed that the crystal structure and the (Sb<sub>4</sub>Se<sub>6</sub>)<sub>n</sub> ribbon orientation of Sb<sub>2</sub>Se<sub>3</sub> obtained by RF sputtering were strongly dependent on the deposition temperature and type of substrate. The authors tested different types of substrate/underlayers (glass, Mo, FTO, CdS, and ZnO) observing a thermodynamical grain alignment along the (001) direction, vertical with respect to the substrate, for depositions at 300 °C on thick samples grown on CdS ( $\Sigma$  TC (hkℓ) (ℓ ≠ 0) = 91%) and ZnO ( $\Sigma$  TC (hkℓ) (ℓ ≠ 0) = 80%). An efficiency of 2.36% was reached, with a J<sub>sc</sub> of 27.06 mA/cm<sup>2</sup> for a

Au/Sb<sub>2</sub>Se<sub>3</sub>/CdS/FTO/glass superstrate configuration solar cell while the PCE was very poor for the absorber grown on Mo substrates.

I. Caño et al. [58] obtained Sb<sub>2</sub>Se<sub>3</sub> layers on Mo-sputtered SLG substrates by a selenization of thermally evaporated Sb. The (002) (vertical ribbons) reflection was predominant for Se-rich conditions, while in Sb-rich conditions, the (231), (141), and (221) peaks became dominant. In detail, with 0.36 Se, a slightly poor Se compound, (002) reflections practically disappeared, while Se-rich conditions could also reduce the V<sub>Se</sub>-type defects and thus improve the device performance.

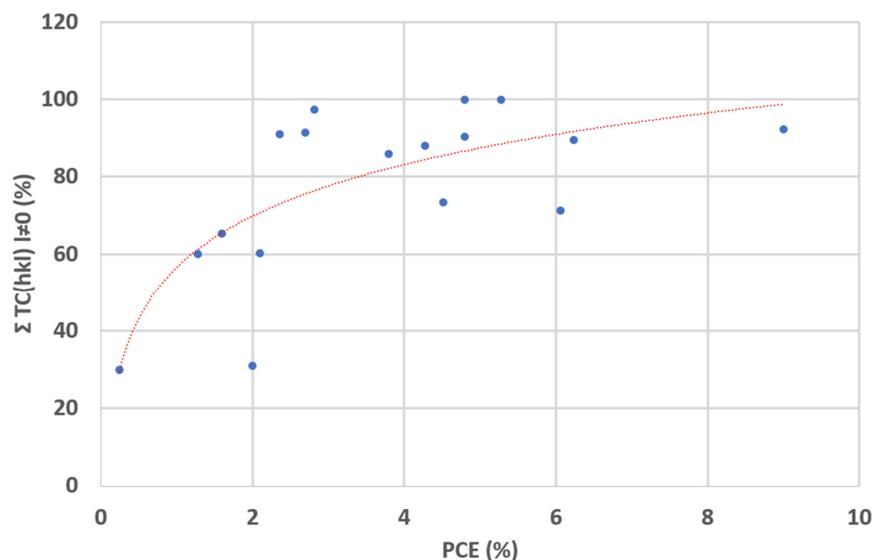
Y. Yang et al. [59] fabricated a Au/Sb<sub>2</sub>Se<sub>3</sub>/CdSe/FTO/glass solar cell by obtaining CdSe and Sb<sub>2</sub>Se<sub>3</sub> both by PLD, with the CdSe/Sb<sub>2</sub>Se<sub>3</sub> bilayer deposited continuously in the same chamber. The authors studied the CdSe temperature influence on Sb<sub>2</sub>Se<sub>3</sub> quality, maintaining a deposition temperature of Sb<sub>2</sub>Se<sub>3</sub> at 500 °C and varying the CdSe temperature: when it is increased to 300 °C, the TCs of the (221) and (221) orientations increased, while the (120)- and (230)-orientation TCs decreased, showing a 1D preferential growth for these conditions. Au/Sb<sub>2</sub>Se<sub>3</sub>/CdSe/FTO/glass solar cells exhibited a J<sub>sc</sub> of 20.18 mA/cm<sup>2</sup> and a PCE of 3.65% for a CdSe deposition temperature of 300 °C.

PLD growth of Sb<sub>2</sub>Se<sub>3</sub> films deposited on CdS/FTO/glass was performed by K. Yang et al. [30] at a substrate temperature of 500 °C, a repetition rate of 6 Hz, and a pulse energy of 90 mJ. The samples showed a preferred direction of (221) and a J<sub>sc</sub> of 31.68 mA/cm<sup>2</sup>, and an efficiency of 4.77% was achieved.

In the only paper (to date) reporting on PED deposition, the role of the substrate was crucial for the 1D ribbon vertical alignment; in fact, F. Pattini et al. [32] showed that the best ribbon alignment for Sb<sub>2</sub>Se<sub>3</sub> grown on FTO/glass ( $\Sigma$  TC (hk $\ell$ ) ( $\ell \neq 0$ ) = 60.2%), while for CdS, this value decreased to 38.4% and, differently, ribbons were completely laid on the substrate surface when Sb<sub>2</sub>Se<sub>3</sub> was grown on Mo ( $\Sigma$  TC (hk $\ell$ ) ( $\ell = 0$ ) = 99.4%). As a consequence, a very low J<sub>sc</sub> was obtained for Sb<sub>2</sub>Se<sub>3</sub> deposited on Mo, while AZO/ZnO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/FTO/glass solar cells exhibited a J<sub>sc</sub> of 20.28 mA/cm<sup>2</sup> and a PCE of 2.1% under frontal illumination and an equivalent 3.1% conversion efficiency for a bifacial illumination.

S-N. Park et al. [43] applied a co-evaporation method with Sb<sub>2</sub>Se<sub>3</sub> and Se sources to obtain an Sb<sub>2</sub>Se<sub>3</sub> absorber for solar cells and observed that the fine control of process temperature was extremely crucial; in fact, (hk1)-oriented Sb<sub>2</sub>Se<sub>3</sub> ribbons were favored when the substrate was heated in the range between 270 °C and 315 °C; in particular, rod arrays preferentially oriented along (hk1) were obtained for 315 °C, while 330 °C stimulated the growth of hk0 planes. In these conditions, an extrapolated  $\Sigma$  TC (hk $\ell$ ) ( $\ell \neq 0$ ) was 73.5%. The authors proposed a nucleation and growth model for explaining the influence of the substrate temperature on the thin film formation, in particular, the evolution of Sb<sub>2</sub>Se<sub>3</sub> from flat to rods with the increasing substrate temperature, based on a Terrace–Ledge–Kink model. The (001), (211), and (221) surfaces presented higher surface energies than (100), (010), (110), and (120), which had no dangling bonds and tended to form terraces. On the other hand, (hk1) surfaces had large numbers of dangling bonds and presented many kink and ledge sites. Increasing temperatures and consequently the diffusion length stimulated the adatom to migrate to these sites. As the propagation direction was expected to be (001) because of the large number of dangling bonds, a growth of rods along the vertical direction was predicted. The rod array obtained at 315 °C implied a highest PCE of 4.5% and a J<sub>sc</sub> of 25.39 mA/cm<sup>2</sup> for Au/AZO/ZnO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/Mo solar cells.

A summary of the reviewed deposition techniques, the TC values, different solar cell architectures, and the correlated performances obtained is reported in Table 1. In Figure 6, the extrapolated  $\Sigma$  TC (hk $\ell$ ) ( $\ell \neq 0$ ) values are plotted as a function of PCE for different solar cells. Even though the points are slightly scattered, a clear trend between TC and PCE can be observed. Even if the PCE value also depends on other electrical parameters, on the different HTL and ETL materials, and even on the peculiar deposition method, one can argue that high-efficiency cells must have a high degree of vertical ribbon orientation.



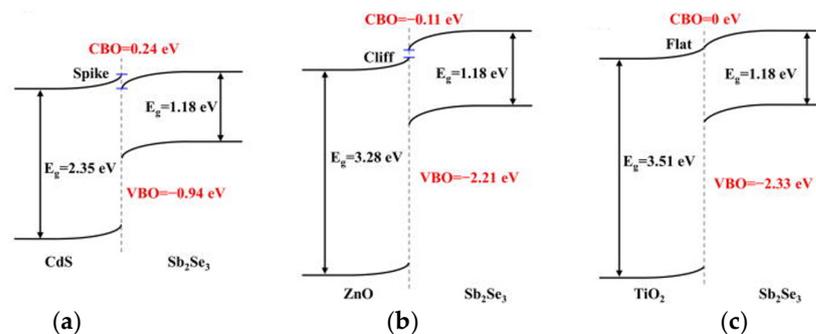
**Figure 6.** Extrapolated  $\Sigma TC(hk\ell)$  ( $\ell \neq 0$ ) values versus PCE.

### 3.2. HTL/ETL, Interfacial Engineering, and Band Alignment

$V_{oc}$  in  $Sb_2Se_3$  solar cells is strongly affected by the interface and SRH recombination. In order to recover  $V_{oc}$  losses, the optimization of the band alignment is fundamental to suppress the interface and defect recombination. In semiconductors, offsets between conduction bands and valence bands at the interfaces of the heterostructures are fundamental for the good working of solar cells. A minimization of the band offset should be achieved, and a “spike-like” configuration is more adequate, where the offset is positive, hence the conduction band minimum of the absorber is lower than the conduction band minimum of the buffer/window layer [60]. The choice of ETLs and HTLs controls the energy band alignments in  $Sb_2Se_3$  solar cells. Different ETLs and HTLs have been explored in the literature to find the optimal solar cell configuration.

#### 3.2.1. ETLs

Among ETLs, CdS is largely used as it is commonly employed as a buffer layer in CIGS, CdTe, and CZTSSe solar cells and it is easily obtained by CBD. The conduction band offset (CBO) at the CdS/ $Sb_2Se_3$  interface [61] is a type-II band alignment, the corresponding calculated CBO and valence band offset (VBO) at the CdS/ $Sb_2Se_3$  interface are 0.24 and 0.94 eV, respectively (Figure 7). However, Cd-free ETLs are objects of study to avoid the toxicity of Cd and other drawbacks associated with CdS, such as a high lattice mismatch (>10%) with  $Sb_2Se_3$ , undesired absorption, the need for surface treatments, and the Cd interdiffusion at the  $Sb_2Se_3$ /CdS interface which causes further defects [62].



**Figure 7.** Band alignments between  $Sb_2Se_3$  and different buffer layers—CdS (a), ZnO (b), and  $TiO_2$  (c). Reproduced from [61], with the permission of AIP Publishing.

On the other hand, SnO<sub>2</sub>, TiO<sub>2</sub>, and ZnO, have similar lattice parameters with Sb<sub>2</sub>Se<sub>3</sub>. These kind of ETLs have been predominantly explored in superstrate configurations. The ZnO/Sb<sub>2</sub>Se<sub>3</sub> interface presents a cliff-type CBO of 0.11 eV and a VBO of 2.21 eV, while TiO<sub>2</sub>/Sb<sub>2</sub>Se<sub>3</sub> present a flat interface for CBO and a VBO of 2.33 eV [61]. S. Lu et al. conclude that a promising strategy would be to combine CdS and TiO<sub>2</sub> with Sb<sub>2</sub>Se<sub>3</sub> in order to obtain a favorable spikelike band alignment.

Alternative ETLs, investigated in theoretical studies are WS<sub>2</sub> [63], CdZnS [64], CdS-3N, ZnMgO [65], and ZnSe [66].

CdS as an ETL has been investigated by several groups in Sb<sub>2</sub>Se<sub>3</sub> solar cells. More recently, modified CdS layers were studied for interface engineering, to modify the CdS/Sb<sub>2</sub>Se<sub>3</sub> heterojunction from a “cliff-like” structure to a “spike-like” structure. Y. Luo et al. [67] obtained an Al<sup>3+</sup> cation doping in the CdS buffer layer (ETL) through spin-coating and postannealing methods. The Al doping allowed the optimization of the band alignment with an ideal CBO, modifying it from a “cliff-like” structure to a “spike-like” one, thus reducing the charge recombination. Sb<sub>2</sub>Se<sub>3</sub> was obtained by Sb RF-MS deposition and subsequent selenization while the Al-doped CdS film was obtained via direct current (DC) MS. Solar cells with a Ag/ITO/CdS:Al/Sb<sub>2</sub>Se<sub>3</sub>/Mo structure achieved a PCE of 8.41%, J<sub>sc</sub> = 28.26 mA cm<sup>-2</sup>, V<sub>oc</sub> = 489 mV, and FF = 60.87%.

In another work, a CdS ETL was also treated by using nontoxic SbCl<sub>3</sub> to form an Sb-CdS/Sb<sub>2</sub>Se<sub>3</sub> interface [68], which also produced a “spike”-like-type heterojunction. A Au/spiro-OMeTAD/Sb<sub>2</sub>Se<sub>3</sub>/CdS/FTO/glass superstrate structure delivered a PCE of 6.13%, while with a normal CdS/Sb<sub>2</sub>Se<sub>3</sub> interface, the PCE was 3.95%. The authors observed that this SbCl<sub>3</sub> treatment induced the formation of pure hexagonal CdS which stimulated the growth of an Sb<sub>2</sub>Se<sub>3</sub> film with a (hk1) preferential orientation.

J. Cheng et al. fabricated a Cd(S,O) ETL [69] through a sol-gel method; the oxygen content was controlled using an anhydrous spin solution. The possibility of changing the Cd/S content ratio permitted the optimization of the CdS layer properties. A Au/Sb<sub>2</sub>Se<sub>3</sub>/CdS(O)/ITO solar cell structure reached an improved efficiency of 5.76% for a Cs:S ratio of 1:0.85.

An oxygenated CdS (CdS:O) ETL was investigated by Y. Liu et al. [70]. CdS:O was obtained by reactive sputtering with a CdS target and an Ar/O<sub>2</sub> mixed working gas, while the Sb<sub>2</sub>Se<sub>3</sub>-absorbed layer by CSS with a thickness between 1200 nm and 1500 nm. An AZO/ZnO/CdS:O/CdS/Sb<sub>2</sub>Se<sub>3</sub>/MoSe<sub>2</sub>/Mo/glass solar cell with an O<sub>2</sub> content of 0.5% in the sputtering environment achieved V<sub>oc</sub> = 408 mV, J<sub>sc</sub> = 28.11 mA cm<sup>-2</sup>, FF = 66.98%, and PCE = 7.69%.

L. Guo et al. [71] also studied CdS:O obtained by RF sputtering as an ETL for Sb<sub>2</sub>Se<sub>3</sub>-based solar cells grown by CSS. Sputtered CdS:O exhibited a better quality than CdS deposited by CBD; the preferred grain orientation was (211) in CdS:O/Sb<sub>2</sub>Se<sub>3</sub>, while it was (221) in CBD CdS/Sb<sub>2</sub>Se<sub>3</sub>. Oxygen also played a role in blocking the interdiffusion of Cd into the Sb<sub>2</sub>Se<sub>3</sub> film. Thus, the PCE was increased from 6.1 to 7% from a CBD CdS to a sputtered CdS:O in the Ag/graphite/Sb<sub>2</sub>Se<sub>3</sub>/CdS:O/FTO/glass solar cell configuration.

X. Mao et al. [72] employed a CdS/SnO<sub>2</sub> ETL in a Au/Spiro-OMeTAD/Sb<sub>2</sub>(S,Se)<sub>3</sub>/CdS/SnO<sub>2</sub>/FTO/glass solar cell, achieving a PCE of 8%. In their work, they highlighted the importance of synthesis and specifically the ratio between SnO<sub>2</sub> hydrosol and deionized water during a spin-coating method on the performance of the cells.

G. Li et al. [73] studied a CdZnS ETL, for a ZnO:Al/ZnO/Cd<sub>x</sub>Zn<sub>1-x</sub>S/Sb<sub>2</sub>Se<sub>3</sub>/Mo/glass solar cell with a Cd<sub>0.75</sub>Zn<sub>0.25</sub>S buffer layer. They obtained an efficiency of 6.71%, compared to the CdS/Sb<sub>2</sub>Se<sub>3</sub>-based cell that achieved a PCE of 5.08%. The optimum concentration allowed the formation of a spikelike interface with a CBO of 0.34 eV, which reduced the photocarrier recombination.

SnO<sub>2</sub> has been studied as a valid alternative to CdS thanks to the interesting band alignment with Sb<sub>2</sub>Se<sub>3</sub> (spikelike heterojunction) and high electron mobility. J. Zhou et al. [74] studied SnO<sub>2</sub>, obtained by a spin-coating method, treated with CdCl<sub>2</sub> as an ETL for Sb<sub>2</sub>Se<sub>3</sub> cells. They observed that the CdCl<sub>2</sub> treatment was fundamental to grow

vertically oriented  $\text{Sb}_2\text{Se}_3$  ribbons; in fact, efficiency improved strongly from 0.12 to 4.76% when  $\text{SnO}_2$  was treated in a C/P3HT/ $\text{Sb}_2\text{Se}_3$ / $\text{SnO}_2$ /FTO/glass solar cell.

W. Wang et al. [40] explored a double interface  $\text{SnO}_2$ / $\text{TiO}_2$ /CdS ETL for VTD-grown  $\text{Sb}_2\text{Se}_3$  in a superstrate configuration, obtaining a 7% PCE, as already mentioned.

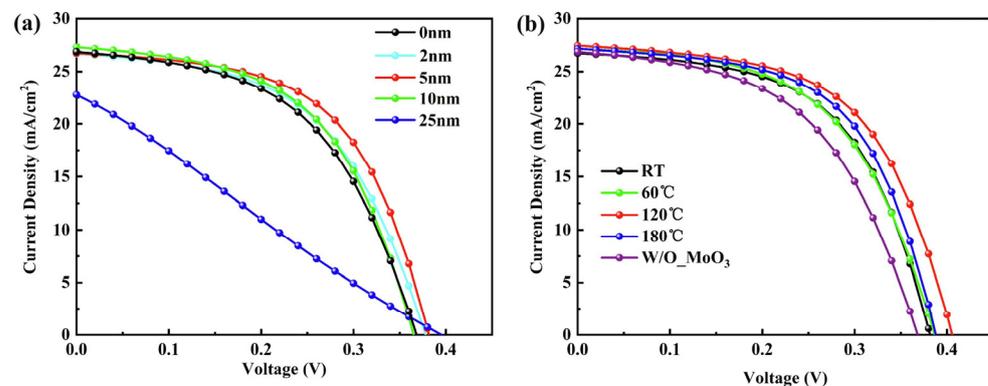
S. Wen et al. [75] also showed the importance of the  $\text{CdCl}_2$  treatment on a  $\text{SnO}_2$  ETL in a Au/ $\text{Sb}_2\text{Se}_3$ / $\text{SnO}_2$ /ITO/glass solar cell measuring efficiency increases from 2.02 to 4.03% when the treatment was performed.

Z. Chen et al. [76] studied La-doped  $\text{SnO}_2$  as an ETL, obtaining an efficiency of 3.25% for Au/ $\text{Sb}_2\text{Se}_3$ / $\text{SnO}_2$ /FTO/glass solar cells. The authors observed that La doping improved the crystallinity and electrical conductivity of  $\text{SnO}_2$  films.

$\text{CdCl}_2$  treatment was also investigated by Y. Wang et al. [77], this time on  $\text{TiO}_2$ . The importance of this treatment was clear since the  $\text{Sb}_2\text{Se}_3$  device's PCE improved from 2.02 to 6.06% with the Au/Spiro-OMeTAD/ $\text{Sb}_2\text{Se}_3$ / $\text{TiO}_2$ /FTO/glass device structure when  $\text{CdCl}_2$  was used on  $\text{TiO}_2$ . As a consequence of the treatment, the CBO of the  $\text{Sb}_2\text{Se}_3$ / $\text{TiO}_2$  heterojunction reduced from 0.50 to 0.20 eV producing a narrower clifflike CBO of the  $\text{Sb}_2\text{Se}_3$ / $\text{TiO}_2$  heterojunction, which favored a passivated interface recombination and facilitated the electron transportation from  $\text{Sb}_2\text{Se}_3$  to  $\text{TiO}_2$ .

X. Wang et al. [78] fabricated Au/ $\text{Sb}_2\text{Se}_3$ / $\text{CeO}_2$ /CdS/FTO/glass solar cells, exploring ultrathin cerium dioxide ( $\text{CeO}_2$ ) obtained by evaporation, together with CdS as ETLs. A  $\text{CeO}_2$  layer of 2 nm stimulated the (221) orientation in  $\text{Sb}_2\text{Se}_3$  ribbons and the solar cell exhibited a 5.14% PCE. The authors attributed the increase in PCE to an improvement in crystallinity and a reduction in photocarrier recombination at the interface between  $\text{Sb}_2\text{Se}_3$  and CdS, due to the larger (3.2 eV) energy gap of  $\text{CeO}_2$ .

J. Zhang et al. [79] used an n-type  $\text{MoO}_3$  layer as the ETL obtaining a 6.3% conversion efficiency in a Au/ $\text{MoO}_3$ / $\text{Sb}_2\text{Se}_3$ /CdS/FTO/glass superstrate solar cells, optimizing  $\text{MoO}_3$ 's thickness and substrate temperature during its deposition (Figure 8).



**Figure 8.** J–V curves of solar cells with (a) different thickness of  $\text{MoO}_3$  layers, (b) different substrate temperatures during deposition of 5 nm  $\text{MoO}_3$ . Reproduced with permission from [79], ©2021 Elsevier B.V.

Alternative Cd-free solar cells have been a strategic goal in order to achieve an environmentally sustainable PV technology. W. Wang et al. obtained  $\text{TiO}_2$ / $\text{SnO}_2$  double ETLs, treated with  $\text{SbCl}_3$ , demonstrating a PCE of 5.82% in a Au/ $\text{Sb}_2\text{Se}_3$ / $\text{TiO}_2$ / $\text{SnO}_2$ /ITO/glass solar cell [80].

$\text{Zn}_{1-x}\text{Sn}_x\text{O}$  layers [81] were obtained via magnetron cosputtering as an ETL. The authors obtained a PCE of 3.44% for a Ag/ITO/ZTO/ $\text{Sb}_2\text{Se}_3$ /Mo/glass substrate solar cell, exploiting a  $\text{Zn}_{0.57}\text{Sn}_{0.43}\text{O}$  buffer layer.

Y. Dong et al. [82] investigated a  $\text{ZnCl}_2$ -modified  $\text{In}_2\text{S}_3$  ETL also for a Cd-free solar cell in a Au/Spiro-OMeTAD/ $\text{Sb}_2\text{Se}_3$ / $\text{In}_2\text{S}_3$ /FTO solar cell. A  $\text{ZnCl}_2$  post-treatment favored a quality improvement of the  $\text{In}_2\text{S}_3$  film, prepared by CBD, also inducing a longitudinal growth on the  $\text{Sb}_2\text{Se}_3$  layer, fabricated via VTE. Thus, on  $\text{InCl}_2$ - $\text{In}_2\text{S}_3$ ,  $(\text{Sb}_4\text{Se}_6)_n$  ribbons

exhibited a perpendicular orientation to the substrate surface. The solar cell PCE increased from 2.63% to 5.00% due to the ZnCl<sub>2</sub> treatment.

ZnSe as an alternative ETL was studied theoretically by R. Kumari et al. with SCAPS-1D and the Al/ZnSe/Sb<sub>2</sub>Se<sub>3</sub>/Mo solar cell efficiency was 24% with optimized parameters [66].

Moreover, an organic ETL was recently studied for Cd-free Sb<sub>2</sub>Se<sub>3</sub>-based solar cells. For example, C60 was used in [83] for an Al/Alq3(3.0 nm)/C60 (5.0 nm)/Sb<sub>2</sub>Se<sub>3</sub> (~50 nm)/NPB (6.0 nm)/ITO/glass solar cell, in which a PCE of 5.03% was demonstrated. In that paper, the NPB (N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine) layer was successfully used to facilitate the Sb<sub>2</sub>Se<sub>3</sub> crystallization, ribbon orientation, and photocarrier recombination suppression.

D. Rovira et al. [84] presented a polymeric ETL in a CdS-free solar cell, with an AZO/b-PEI/ZnO/Sb<sub>2</sub>Se<sub>3</sub>/Mo/glass structure. Sb<sub>2</sub>Se<sub>3</sub> was obtained by the evaporation of 280nm-thick Sb film on the deposited Mo and a subsequent annealing in a furnace under a selenium atmosphere. The polymeric layer obtained by spin-coating formed interfacial dipoles which contributed to enhance the V<sub>oc</sub> from 243 mV to 344 mV, and a PCE of 2.41% was obtained.

In Table 2, the ETL, HTL, and their effects on the solar cells' parameters are summarized.

**Table 2.** Different materials used as ETL/HTL for Sb<sub>2</sub>Se<sub>3</sub> solar cells and their performance.

ETL	HTL	PCE	Absorber Deposition Method	Reference
CdS:Al	/	8.41%	RF-MS + selenization	[67]
Sb-CdS	SpirOmetad	6.13%	RTE	[68]
Cd(S,O)	/	5.76%	Thermal evaporation	[69]
CdS:O	MoSe <sub>2</sub>	7.69%	CSS	[70]
CdS/SnO <sub>2</sub>	SpirOmetad	8%	Hydrothermal	[72]
CdZnS	/	6.71%	CSS	[73]
CdS	/	5.08%	CSS	[73]
SnO <sub>2</sub>	P3HT	4.76%	CSS	[74]
CdS/TiO <sub>2</sub> /SnO <sub>2</sub>	/	7%	VTD	[40]
CdS/TiO <sub>2</sub>	/	5.82%	VTD	[80]
SnO <sub>2</sub>	/	4.03%	VTD	[75]
La-SnO <sub>2</sub>	/	3.25%	RTE	[76]
TiO <sub>2</sub> (CdCl <sub>2</sub> treatment)	SpirOmetad	6.06%	Thermal evaporation	[77]
MoO <sub>3</sub>	CdS	6.3%	RTE	[79] Figure 8
ZTO	/	3.44%	Magnetron cosputtering	[81]
InCl <sub>2</sub> -In <sub>2</sub> S <sub>3</sub>	SpirOmetad	5.0%	VTE	[82]
C60	NPB	5.03%	VTE	[83]
CdS	CuSCN	7.5%	VTD	[85]
CdS	WO <sub>3-x</sub> /	7.1%	CSS	[86]
CdS/TiO <sub>2</sub>	MoSe <sub>2</sub>	9.2%	CSS	[25] Figure 5b
CdS	MoSe <sub>2</sub>	10.12%	IVD	[29] Figure 2d
CdS:O	/	7%	CSS	[71]
CeO <sub>2</sub>	/	5.14%	RTE	[78]
CdS	NiO <sub>x</sub>	6.5%	VTD	[87]
SnO <sub>2</sub> /CdS	t-Se	7.45%	CSS	[34]
CdS	MoS <sub>3</sub>	6.65%	TE	[88]
CdS	MoO <sub>2</sub>	8.14%	RF-MS + selenization	[89]
CdS	CuSbSe <sub>2</sub>	5.87%	VTD	[90]

Table 2. Cont.

ETL	HTL	PCE	Absorber Deposition Method	Reference
CdS	Mo/PbSe	8.4%	CSS	[91]
TiO <sub>2</sub>	PCDTBT	6.6%	CSS	[92]
TiO <sub>2</sub>	P3HT	6.88%	CSS	[93]
CdS	SpirOmetad	7.27%	VTD	[94]

### 3.2.2. HTLs

Many hole transport layer (HTL) materials, both inorganic and organic, have been investigated and are still being explored for Sb<sub>2</sub>Se<sub>3</sub> solar cells. Inorganic HTLs have the advantage of being stable and generally having higher carrier mobilities, while organic HTLs can be easily processed by printing (inkjet, roll-to-roll) in flexible organic PV.

Y. Cao et al. [95] theoretically studied inorganic hole transport materials such as Cu<sub>2</sub>O, CuI, and NiO for Ag/ETL/Sb<sub>2</sub>Se<sub>3</sub>/HTL/ITO/glass architectures. With the proper absorber thickness, HTL acceptor concentration, and hole mobility, NiO as an HTL and PCBM as an ETL, the authors calculated a theoretical 24.7% efficient device.

A. Sunny et al. [96] proposed an Al/FTO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/SnS/Mo structure, with a SnS HTL and a CdS ETL, they calculated by 1D (SCAPS-1D) simulation software an interesting PCE of 29.89%.

S. Campbell et al. [97] theoretically studied MoO<sub>x</sub> and NiO HTLs in Sb<sub>2</sub>Se<sub>3</sub> solar cells. They observed that for CSS-grown superstrate solar cells, a NiO HTL was more adequate than MoO<sub>x</sub> since J<sub>sc</sub> was enhanced by 40% compared to reference and MoO<sub>x</sub>-based devices. In addition, they observed that NiO layers facilitated a vertical ribbon orientation growth.

NiO<sub>x</sub> and Ni as an HTL and alternative back contact, respectively, were investigated by J. Zhang et al. [87]. The structure with a 7 nm thick NiO<sub>x</sub> exhibited the best PCE of 6.5%.

K. Li et al. [85] investigated CuSCN as an HTL for Sb<sub>2</sub>Se<sub>3</sub> solar cells achieving a 7.5% efficiency in CuSCN/Sb<sub>2</sub>Se<sub>3</sub>/CdS/ITO/glass structure solar cells. In this case, the strong polarity in the Cu–C–N–S chains along the *c*-axis induced the desired vertical preferential growth. Next, moderate thermal treatments (in particular 85 °C for 10 min) of CuSCN also favored a Cu ion diffusion into Sb<sub>2</sub>Se<sub>3</sub> causing a grain boundary inversion and the increase in Cu vacancies in CuSCN, thus enhancing the doping density of CuSCN.

C. Liu et al. [86] investigated spin-coated WO<sub>3-x</sub> as an HTL for an Sb<sub>2</sub>Se<sub>3</sub> absorber deposited by CSS, and their solar cells reached a PCE of 7.1% in Sb<sub>2</sub>Se<sub>3</sub> solar cells as n-i-p devices fabricated with the structure of Au/WO<sub>3-x</sub>/Sb<sub>2</sub>Se<sub>3</sub>/CdS/FTO/glass.

K. Shen et al. [34], as already mentioned, adopted a 2 nm thick trigonal Se (t-Se) film as HTL. They observed a higher open-circuit voltage (V<sub>oc</sub>), which was attributed to the band bending at the Sb<sub>2</sub>Se<sub>3</sub>/t-Se interface. They also observed an increased durability of the solar cells compared to those with a Spiro-OMeTAD HTL (2% vs. 40% efficiency decrease after 40 days). This confirmed the importance of using an inorganic HTL for robust and durable Sb<sub>2</sub>Se<sub>3</sub>-based solar cells.

Y. Ma et al. [88] investigated the use of MoS<sub>3</sub> as a hole extraction and transport layer. Solar cells with the Au/MoS<sub>3</sub>/Sb<sub>2</sub>Se<sub>3</sub>/CdS/FTO/glass configuration exhibited a PCE of 6.65% versus 3.89% in the absence of HTL.

J. Lin et al. [89] investigated a Mo/MoO<sub>2</sub> interface as HTL in a Ag/ITO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/MoO<sub>2</sub>/Mo/glass structure. In that case, Sb<sub>2</sub>Se<sub>3</sub> was obtained by Sb precursor RF sputtering and a post-selenization of the Sb layer. The MoO<sub>2</sub> layer suppressed the formation of the MoSe<sub>2</sub> interface layer, contributing to the interface reaching a very high PCE of 8.14%. The MoO<sub>2</sub> interface layer also induced the growth of (211)-oriented Sb<sub>2</sub>Se<sub>3</sub> with large grains.

Q. Cang et al. [90] exploited CuSbSe<sub>2</sub> as an HTL for a Au/CuSbSe<sub>2</sub>/Sb<sub>2</sub>Se<sub>3</sub>/CdS/FTO solar cell, where the CuSbSe<sub>2</sub> layer was obtained by co-sputtering from Cu and Sb<sub>2</sub>Se<sub>3</sub> targets; a PCE of 5.87% was obtained in comparison with 4.36% without HTL. CuSbSe<sub>2</sub> contributed to enhancing the carrier concentration and reducing the photocarrier recombination associated with the ultrathin CuSbSe<sub>2</sub> layer.

A modified HTL was studied by et al. [91] with a PbSe layer evaporated at room temperature at the solar cell back contact interface with Mo. The authors observed that PbSe simultaneously facilitated the growth of Sb<sub>2</sub>Se<sub>3</sub> crystals obtained by CSS with an enhanced (hk1) orientation and hole extraction at the Sb<sub>2</sub>Se<sub>3</sub>/Mo interface. The effect was attributed to the reduction in deep-level traps by Pb into the Sb<sub>2</sub>Se<sub>3</sub> and to the formation of a blocking barrier by PbSe, contributing to reducing the carrier recombination. An 8.4% efficient Sb<sub>2</sub>Se<sub>3</sub> solar cell was achieved for Ag/AZO/ZnO/CdS/Sb<sub>2</sub>Se<sub>3</sub>/PbSe/Mo fabricated on a flexible polyimide film (PI) substrate.

Pasini et al. [98] investigated a Fe-S-O HTL deposited at RT by RF-MS. The solar cell structure Sb<sub>2</sub>Se<sub>3</sub>/ZnCdS/glass with contact strips of Fe-S-O covered by Au was reported with a PCE between 5% and 6%.

Alternatives to organic HTLs have been extensively studied for Sb<sub>2</sub>Se<sub>3</sub>-based solar cells, showing interesting improvements in PV performance in the last years. O. S. Hutter et al. [92] used a TiO<sub>2</sub> layer as ETL and poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), obtained by spin-casting, as HTL achieving an interesting 6.6% efficiency for a Au/PCDTBT/Sb<sub>2</sub>Se<sub>3</sub>/TiO<sub>2</sub>/FTO/glass structure where the Sb<sub>2</sub>Se<sub>3</sub> absorber was obtained by CSS and a seed layer method.

Another important organic material, P3HT, has been studied in several works as HTL [74,93]. In the case of C. H. Don et al. [93], it was deposited by spin-coating in a Au/P3HT/Sb<sub>2</sub>Se<sub>3</sub>/TiO<sub>2</sub>/FTO device, achieving a PCE of 6.88%.

Spiro-OMeTAD as HTL has been employed in several works [68,72,77,82,94]. Z. Cao et al. [94] recently investigated Spiro-OMeTAD as HTL and CdS as ETL. In this case the Sb<sub>2</sub>Se<sub>3</sub> absorber was fabricated by the VTD method. The authors highlighted the importance of pumping excess oxygen out of the furnace tube, removing oxygen from the CdS/Sb<sub>2</sub>Se<sub>3</sub> interface to both decrease the defect concentration and enhance the (hkℓ, ℓ = 1)-oriented ribbon growth. In this way, Au/Spiro-OMeTAD/Sb<sub>2</sub>Se<sub>3</sub>/CdS/ITO solar cells achieved an efficiency of 7.27%.

### 3.3. Doping

Undoped Sb<sub>2</sub>Se<sub>3</sub> generally presents a low intrinsic p-type charge carrier density ( $\sim 10^{13} \text{ cm}^{-3}$ ), which induces a small built-in potential, and thus a limited  $V_{oc}$ . However, it is also difficult to extrinsically dope Sb<sub>2</sub>Se<sub>3</sub> because the doping elements often remain located between the conductive ribbons, where they are not active, and not into the lattice [10].

On the other hand, external doping in Sb<sub>2</sub>Se<sub>3</sub> has been used to passivate or suppress defects, such as  $V_{Se}$  defects or grain boundaries, especially between the ribbons. This can reduce nonradiative recombination and improve  $V_{oc}$ .

The latter is the case of Na doping that was investigated in Sb<sub>2</sub>Se<sub>3</sub>-based solar cells by Y. Li et al. [99]. The authors found a negligible influence on the conductivity of the Sb<sub>2</sub>Se<sub>3</sub> layer, arguing that Na diffused in the film and remained inert between (Sb<sub>4</sub>Se<sub>6</sub>)<sub>n</sub> ribbons. W-H Li et al. investigated Sb<sub>2</sub>Se<sub>3</sub> doping with PbI<sub>2</sub> by thermal diffusion [100]. A 1 nm thin layer of PbI<sub>2</sub> was deposited on an ITO/glass substrate and then an amorphous Sb<sub>2</sub>Se<sub>3</sub> film was grown on it. I and Pb interdiffusion was then promoted during annealing. Pb<sub>Sb</sub> defects were detected in Sb<sub>2</sub>Se<sub>3</sub>, and Pb acted as a p-dopant, increasing the hole concentration from  $10^9$  to  $10^{13} \text{ cm}^{-3}$ . The authors fabricated ITO/PbI<sub>2</sub>-doped Al/Alq<sub>3</sub>/C60/Sb<sub>2</sub>Se<sub>3</sub> solar cells which exhibited a PCE of 4.43%, in comparison with a PCE of 2.87% for the undoped Sb<sub>2</sub>Se<sub>3</sub>-based cells.

M. Huang et al. [101] also investigated Pb doping in Sb<sub>2</sub>Se<sub>3</sub>. They reached a hole concentration of  $10^{16} \text{ cm}^{-3}$  also observing that Pb doping induced shallow defects corresponding to Pb<sub>Sb</sub>.

Y. Ma et al. [102] studied tellurium-doped Sb<sub>2</sub>Se<sub>3</sub> to reduce deep-level defects. In particular, the authors obtained Se-rich Sb<sub>2</sub>Se<sub>3</sub> layers, limiting  $V_{Sb}$  and  $Se_{Sb}$  defects. This was also observed in works where the importance of selenization, also able to tailor the Se/Sb ratio to obtain Se-rich films, was clearly highlighted [103].

Cu-doped  $\text{Sb}_2\text{Se}_3$  was presented by G. Spaggiari et al. [104] for  $\text{Sb}_2\text{Se}_3$  obtained by LT-PED. Cu-doped  $\text{Sb}_2\text{Se}_3$  free-carrier concentration was estimated in the order of  $10^{15} \text{ cm}^{-3}$  and successfully increased by about two orders of magnitude with respect to the undoped  $\text{Sb}_2\text{Se}_3$ .

Y. Li et al. [105] investigated Mg and Fe doping in  $\text{Sb}_2\text{Se}_3$ . The authors found that while Mg was predominately inert to the electric properties of  $\text{Sb}_2\text{Se}_3$ , Fe produced n-type doping even if the electron-free density was still low, around  $10^{13} \text{ cm}^{-3}$ . These extrinsic defects were also associated with deep levels, which are detrimental for solar cell applications.

As already mentioned, H. Guo et al. [26] introduced KOH to the surface of  $\text{Sb}_2\text{Se}_3$  films, improving the doping density from  $10^{13}$  to  $10^{15} \text{ cm}^{-3}$ , which contributed to enhance the solar cell performance (PCE of 7.16%).

X. Liu et al. [106] observed that in  $\text{Sb}_2\text{Se}_3$  material, intrinsic defect acceptors  $\text{Se}_{\text{Sb}}$  and  $\text{V}_{\text{Sb}}$  formed preferentially in Se-rich conditions, while deep donors  $\text{V}_{\text{Se}}$  and  $\text{Sb}_{\text{Se}}$  were dominant in Se-poor compounds. The authors provided an in situ compensating process with Se vapor supplied during the growth, obtaining Se-rich conditions, and producing a higher film conductivity, shallower defects, and a longer carrier lifetime.

T. D. C. Hobson et al. [107] used  $\text{MgCl}_2$  to n-dope  $\text{Sb}_2\text{Se}_3$  demonstrating that chlorine was a substitutional shallow n-dopant with  $10^{16}$ – $10^{17} \text{ cm}^{-3}$  of doping density. Solar cells based on this n-type absorber demonstrated a PCE of 7.3%.

T. D. C. Hobson et al. [108] also obtained p doping, with a carrier density of  $7.4 \times 10^{14} \text{ cm}^{-3}$ , introducing Sn in  $\text{Sb}_2\text{Se}_3$  layers. Sn substitutionally replaced Sb; however, the introduced Sn atom concentration was  $7 \times 10^{18} \text{ cm}^{-3}$ , much higher than the net carrier density, probably because of the Fermi level pinning.

Sn doping was also investigated by S. Chen et al. [109] in  $(\text{Sn}_x\text{Sb}_{1-x})_2\text{Se}_3$  with x ranging from 0 to 0.1. P-type doping was identified, and electrical conductivity was improved by more than three orders of magnitude in comparison with the undoped samples.

Fe-doped  $\text{Sb}_2\text{Se}_3$  was obtained in electrodeposited samples [110], with a hole density three orders of magnitude higher than the undoped films.

H. Zhou et al. [111] explored S doping of  $\text{Sb}_2\text{Se}_3$  nanowire arrays with a gradient of its concentration whose characteristics allowed the formation of a cascade band structure, the improvement of the charge carrier transport, and consequently the increase in the solar cell fill factor. In [112], the authors also investigated S-doped  $\text{Sb}_2\text{Se}_3$  (obtained by an electrodeposition method) increasing the p doping of  $2.17 \times 10^{16} \text{ cm}^{-3}$  in the undoped sample to  $5.63 \times 10^{18} \text{ cm}^{-3}$  in the S-doped one.

Silver doping has been studied by S. Gautam et al. [113], who observed that Ag doping of  $\text{Sb}_2\text{Se}_3$  presented a dual nature dependent on the temperature. In particular, at low temperatures, Ag showed an activation energy close to undoped material, while at higher temperatures, the activation energy decreased to 0.26 eV.

Ni doping of  $\text{Sb}_2\text{Se}_3$  also promotes p-conduction type [114] and its effect in enhancing the broadband in photodetector based on a nanowire array has been investigated.

Bi doping of  $\text{Sb}_2\text{Se}_3$  permitted to achieve an n-doping density of around  $10^{19} \text{ cm}^{-3}$  in samples obtained by electrodeposition [115].

S. Chen et al. [116] investigated Pt doping of  $\text{Sb}_2\text{Se}_3$  through a Pt metallic interlayer between  $\text{Sb}_2\text{Se}_3$  and the CdS layer. Pt generated a p-doping increase of one order of magnitude (to  $3.93 \times 10^{15} \text{ cm}^{-3}$ ) in relation to the undoped sample. The authors also observed a deep-level passivation and an oxygen contamination reduction effect of the formed  $\text{PtSe}_2$  layer, which, concurrently with doping, contributed to enhance the PCE from 5.58 to 7.49% in the Ag/ITO/CdS/ $\text{Sb}_2\text{Se}_3$ :Pt/Mo/glass solar structure.

Te-doped  $\text{Sb}_2\text{Se}_3$  film by a co-post-selenization treatment was investigated by G. Chen et al. [117]. Firstly, an RF-MS deposition method was used to obtain the Sb metallic precursors thin films, then a post-selenization doping treatment was performed in a vacuum tubular furnace with Te and Se powder sources. Te- $\text{Sb}_2\text{Se}_3$  thin films with a preferred (hk1) orientation was successfully obtained and the Ag/ITO/CdS/Te- $\text{Sb}_2\text{Se}_3$ /Mo solar cell achieved a PCE of 7.61% efficiency.

#### 4. Conclusions

In this paper, we summarized the latest research on the grain orientation, ETL and HTL configurations, and doping of planar  $\text{Sb}_2\text{Se}_3$ -based solar cells fabricated using physical deposition techniques. We focused on the relationship between the deposition conditions and the resulting photovoltaic performance.

The efficiency of  $\text{Sb}_2\text{Se}_3$  solar cells has gradually increased in the last ten years, exceeding 10.5%. This has led to a growing interest in this material as a promising candidate for the thin-film solar cell market. Advances in fabrication methods, control of ribbon orientation, defect suppression, and passivation have certainly contributed to the rapid improvement of photovoltaic performance. However, several issues, such as  $V_{oc}$  losses associated with nonradiative recombination defects and effective external doping, remain under investigation and have not been fully resolved.

Among the deposition methods, high-rate growth processes, such as CSS, RTE, IVD, and VTD, have shown the most promising results (PCE > 9–10%) for  $\text{Sb}_2\text{Se}_3$  absorber layers in terms of vertical ribbon alignment. This is a fundamental characteristic for obtaining a material with high conductivity. Other physical deposition techniques (PDTs), such as RFMS, which have recently achieved a PCE > 8%, also appear to be very promising in terms of results and scalability. For ETLs and HTLs, new strategies in interface band alignments and inorganic (especially Cd-free) ETLs such as  $\text{CeO}_2$ ,  $\text{TiO}_2$ , and  $\text{SnO}_2$  (also combined in bi- or trilayers) and HTLs such as  $\text{NiO}_x$ ,  $\text{CuSCN}$ ,  $\text{WO}_{3-x}$ , and  $\text{MoS}_3$  appear as very promising candidates for new configurations of solar cells.

Among the possible dopants for  $\text{Sb}_2\text{Se}_3$  absorber layers, K, Cu, Sn, and Pb have been explored with some success. However, passivation, surface processes, and postdeposition treatments (chemical or thermal) are still open challenges that need to be addressed to further improve the properties of  $\text{Sb}_2\text{Se}_3$ -based devices and their power conversion efficiency (PCE).

**Author Contributions:** Conceptualization, R.J.; methodology, R.J.; validation, G.S. and F.P.; formal analysis, R.J.; investigation, R.J.; resources, S.R.; data curation, F.P.; writing—original draft preparation, R.J.; writing—review and editing, S.R., G.S. and F.P.; visualization, G.S.; supervision, F.P.; project administration, S.R.; funding acquisition, S.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Italian Ministry of the Environment and the Energy Security: Research Fund for the Italian Electrical System (type-A call, published on G.U.R.I. n. 192 on 18 August 2022). The research was also funded by Italian Ministry of University and Research: “Ecosystem for Sustainable Transition in Emilia-Romagna” (EcosistER), funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.5—Call for tender No. 3277 of 30 December 2021.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors would like to thank the financial support of Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) Project PROCAD Defesa DRI 15/2019. This study is a result of the research project “nuovi Concetti, materiali e tecnologie per l’integrazione del fotovoltaico negli edifici in uno scenario di generazione diffusa” (CANVAS), funded by the Italian Ministry of the Environment and the Energy Security, through the Research Fund for the Italian Electrical System (type-A call, published on G.U.R.I. n. 192 on 18 August 2022). The work is part of the project “Ecosystem for Sustainable Transition in Emilia-Romagna” (EcosistER), funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.5—Call for tender No. 3277 of 30 December 2021 of Italian Ministry of University and Research funded by the European Union—NextGenerationEU.

**Conflicts of Interest:** The authors declare no conflict of interest.

## Nomenclature

Ag	Silver
AgSbSe <sub>2</sub>	Silver antimony selenide
Al	Aluminum
Al <sub>2</sub> O <sub>3</sub>	Aluminum(III) oxide
ALD	Atomic layer deposition
Alq <sub>3</sub>	Tris(8-hydroxyquinolino)aluminum, Al(C <sub>9</sub> H <sub>6</sub> NO) <sub>3</sub>
Ar	Argon
Au	Gold
AZO	Aluminum-doped zinc oxide
C <sub>60</sub>	Buckminsterfullerene
CBD	Chemical bath deposition
CBO	Conduction band offset
Cd	Cadmium
CdCl <sub>2</sub>	Cadmium chloride
CdS	Cadmium sulfide
CdS:O	Oxygenated cadmium sulfide
CdTe	Cadmium telluride
CdZnS	Cadmium zinc sulfide
CeO <sub>2</sub>	Cerium(IV) oxide
CIGS, Cu(In,Ga)Se <sub>2</sub>	Copper indium gallium (di)selenide
CIGSSe	Copper indium gallium sulfur selenide
CSS	Close-space sublimation
CuI	Copper(I) iodide
CuInSe <sub>2</sub>	Copper indium selenide
CuSbSe <sub>2</sub>	Copper antimony selenide
CuSCN	Copper(I) thiocyanate
CZ-TA	4,4',4'',4'''-(9-Octylcarbazole-1,3,6,8-tetrayl)tetrakis(N,N-bis(4-methoxyphenyl)aniline)
CZTS	Copper zinc tin sulfide
CZTSSe	Copper zinc tin sulfur selenide
DSSC	Dye-sensitized solar cell
ETL	Electron transport layer
Fe	Iron
FTO	Fluorine-doped tin oxide
HTL	Hole transport layer
I (hkℓ)	Net intensity measured by the experimental XRD patterns after the background subtraction.
I <sub>0</sub> (hkℓ)	Relative intensity of the XRD reflection with (hkℓ) Miller
ITO	Indium tin oxide
IVD	Injection vapor deposition
i-ZnO	Intrinsic zinc oxide
JCPDS	Joint Committee on Powder Diffraction Standards
J <sub>sc</sub>	Short-circuit current density
J-V	Current density-voltage
K	Potassium
KOH	Potassium hydroxide
La	Lanthanum
Mg	Magnesium
MgCl <sub>2</sub>	Magnesium chloride
Mo	Molybdenum
MoSe <sub>2</sub>	Molybdenum(IV) selenide
MoO <sub>3</sub>	Molybdenum trioxide
Ni	Nickel
NiO <sub>x</sub>	Nickel oxide
NPB	N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine
P3HT	Poly(3-hexylthiophene-2,5-diyl)
Pb	Lead

PbI <sub>2</sub>	Lead(II) iodide
Pb <sub>Sb</sub>	Substitutional defect of lead replacing antimony site
PCE	Power conversion efficiency
PCBM	[6,6]-Phenyl-C61-butyric acid methyl ester
PCDTBT	Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]
PDT	Physical deposition techniques
PED	Pulsed electron deposition
PLD	Pulsed laser deposition
Pt	Platinum
PtSe <sub>2</sub>	Platinum diselenide
PV	Photovoltaic
QDs	Quantum dots
RF-MS	Radiofrequency magnetron sputtering
RTE	Rapid thermal evaporation
S	Sulfur
SbCl <sub>3</sub>	Antimony trichloride
Se	Selenium
Sb	Antimony
Sb <sub>Se</sub>	Substitutional defect of antimony replacing selenium site
Se <sub>Sb</sub>	Substitutional defect of selenium replacing antimony site
Sb <sub>2</sub> Se <sub>3</sub>	Antimony triselenide
SL	Seeding layer
SLG	Soda-lime glass
SnO <sub>2</sub>	Tin(IV) oxide
SnS	Tin(II) sulfide
(Sn <sub>x</sub> Sb <sub>1-x</sub> ) <sub>2</sub> Se <sub>3</sub>	Tin-doped antimony selenide
Spiro-OMeTAD	2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene
SRH	Shockley-Read-Hall
TiO <sub>2</sub>	Titanium dioxide, titanium(IV) oxide, titania
TC	Texture coefficient
t-Se	Trigonal selenium
VBO	Valence band offset
V <sub>oc</sub>	Open-circuit voltage
V <sub>Se</sub>	Selenium vacancies
VTE	Vacuum thermal evaporation
VTD	Vapor transport deposition
WO <sub>3-x</sub>	Tungsten oxide
WS <sub>2</sub>	Tungsten disulfide
XRD	X-ray diffraction
ZnO	Zinc oxide
ZnMgO	Zinc magnesium oxide
ZnSe	Zinc selenide
ZTO	Zinc-tin oxide

## References

- Green, M.A.; Dunlop, E.D.; Hohl-Ebinger, J.; Yoshita, M.; Kopidakis, N.; Bothe, K.; Hinken, D.; Rauer, M.; Hao, X. Solar Cell Efficiency Tables (Version 60). *Prog. Photovolt.* **2022**, *30*, 687–701. [[CrossRef](#)]
- Chen, C.; Li, K.; Tang, J. Ten Years of Sb<sub>2</sub>Se<sub>3</sub> Thin Film Solar Cells. *Sol. RRL* **2022**, *6*, 2200094. [[CrossRef](#)]
- Vadapoo, R.; Krishnan, S.; Yilmaz, H.; Marin, C. Electronic Structure of Antimony Selenide (Sb<sub>2</sub>Se<sub>3</sub>) from GW Calculations. *Phys. Status Solidi B* **2011**, *248*, 700–705. [[CrossRef](#)]
- Shockley, W.; Queisser, H.J. Detailed Balance Limit of Efficiency of P-n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32*, 510–519. [[CrossRef](#)]
- Zhao, Y.; Wang, S.; Li, C.; Che, B.; Chen, X.; Chen, H.; Tang, R.; Wang, X.; Chen, G.; Wang, T.; et al. Regulating Deposition Kinetics via a Novel Additive-Assisted Chemical Bath Deposition Technology Enables Fabrication of 10.57%-Efficiency Sb<sub>2</sub>Se<sub>3</sub> Solar Cells. *Energy Environ. Sci.* **2022**, *15*, 5118–5128. [[CrossRef](#)]
- Zhou, Y.; Wang, L.; Chen, S.; Qin, S.; Liu, X.; Chen, J.; Xue, D.-J.; Luo, M.; Cao, Y.; Cheng, Y.; et al. Thin-Film Sb<sub>2</sub>Se<sub>3</sub> Photovoltaics with Oriented One-Dimensional Ribbons and Benign Grain Boundaries. *Nat. Photonics* **2015**, *9*, 409–415. [[CrossRef](#)]

7. Ganose, A.M.; Savory, C.N.; Scanlon, D.O. Beyond Methylammonium Lead Iodide: Prospects for the Emergent Field of  $\text{Ns}^2$  Containing Solar Absorbers. *Chem. Commun.* **2017**, *53*, 20–44. [[CrossRef](#)] [[PubMed](#)]
8. Black, J.; Conwell, E.M.; Seigle, L.; Spencer, C.W. Electrical and Optical Properties of Some  $\text{M}2\text{v}-\text{bN}3\text{vi}-\text{b}$  Semiconductors. *J. Phys. Chem. Solids* **1957**, *2*, 240–251. [[CrossRef](#)]
9. Huang, M.; Xu, P.; Han, D.; Tang, J.; Chen, S. Complicated and Unconventional Defect Properties of the Quasi-One-Dimensional Photovoltaic Semiconductor  $\text{Sb}_2\text{Se}_3$ . *ACS Appl. Mater. Interfaces* **2019**, *11*, 15564–15572. [[CrossRef](#)]
10. Dong, J.; Liu, Y.; Wang, Z.; Zhang, Y. Boosting  $V_{\text{OC}}$  of Antimony Chalcogenide Solar Cells: A Review on Interfaces and Defects. *Nano Sel.* **2021**, *2*, 1818–1848. [[CrossRef](#)]
11. Leng, M.; Luo, M.; Chen, C.; Qin, S.; Chen, J.; Zhong, J.; Tang, J. Selenization of  $\text{Sb}_2\text{Se}_3$  Absorber Layer: An Efficient Step to Improve Device Performance of  $\text{CdS}/\text{Sb}_2\text{Se}_3$  Solar Cells. *Appl. Phys. Lett.* **2014**, *105*, 083905. [[CrossRef](#)]
12. Wang, Y.; Ji, S.; Shin, B. Interface Engineering of Antimony Selenide Solar Cells: A Review on the Optimization of Energy Band Alignments. *J. Phys. Energy* **2022**, *4*, 044002. [[CrossRef](#)]
13. Choi, Y.C.; Mandal, T.N.; Yang, W.S.; Lee, Y.H.; Im, S.H.; Noh, J.H.; Seok, S.I.  $\text{Sb}_2\text{Se}_3$ -Sensitized Inorganic-Organic Heterojunction Solar Cells Fabricated Using a Single-Source Precursor. *Angew. Chem.* **2014**, *126*, 1353–1357. [[CrossRef](#)]
14. Giraldo, S.; Jehl, Z.; Placidi, M.; Izquierdo-Roca, V.; Pérez-Rodríguez, A.; Saucedo, E. Progress and Perspectives of Thin Film Kesterite Photovoltaic Technology: A Critical Review. *Adv. Mater.* **2019**, *31*, 1806692. [[CrossRef](#)] [[PubMed](#)]
15. Kazmerski, L.L.; White, F.R.; Ayyagari, M.S.; Juang, Y.J.; Patterson, R.P. Growth and characterization of thin-film compound semiconductor photovoltaic heterojunctions. *J. Vac. Sci. Technol.* **1977**, *14*, 65. [[CrossRef](#)]
16. Katagiri, H.; Sasaguchi, N.; Hando, S.; Hoshino, S.; Ohashi, J.; Yokota, T. Preparation and evaluation of  $\text{Cu}_2\text{ZnSnS}_4$  thin films by sulfurization of E B evaporated precursors. *Sol. Energy Mater. Sol. Cells* **1997**, *49*, 407. [[CrossRef](#)]
17. Liang, G.-X.; Zhang, X.-H.; Ma, H.-L.; Hu, J.-G.; Fan, B.; Luo, Z.-K.; Zheng, Z.-H.; Luo, J.-T.; Fan, P. Facile Preparation and Enhanced Photoelectrical Performance of  $\text{Sb}_2\text{Se}_3$  Nano-Rods by Magnetron Sputtering Deposition. *Sol. Energy Mater. Sol. Cells* **2017**, *160*, 257–262. [[CrossRef](#)]
18. Tang, R.; Chen, X.-Y.; Liang, G.-X.; Su, Z.-H.; Luo, J.; Fan, P. Magnetron Sputtering Deposition and Selenization of  $\text{Sb}_2\text{Se}_3$  Thin Film for Substrate  $\text{Sb}_2\text{Se}_3/\text{CdS}$  Solar Cells. *Surf. Coat. Technol.* **2019**, *360*, 68–72. [[CrossRef](#)]
19. Spaggiari, G.; Pattini, F.; Bersani, D.; Calestani, D.; De Iacovo, A.; Gilioli, E.; Mezzadri, F.; Sala, A.; Trevisi, G.; Rampino, S. Growth and Structural Characterization of  $\text{Sb}_2\text{Se}_3$  Solar Cells with Vertical  $\text{Sb}_4\text{Se}_6$  Ribbon Alignment by RF Magnetron Sputtering. *J. Phys. D Appl. Phys.* **2021**, *54*, 385502. [[CrossRef](#)]
20. Ma, C.; Guo, H.; Wang, X.; Chen, Z.; Cang, Q.; Jia, X.; Li, Y.; Yuan, N.; Ding, J. Fabrication of  $\text{Sb}_2\text{Se}_3$  Thin Film Solar Cells by Co-Sputtering of  $\text{Sb}_2\text{Se}_3$  and Se Targets. *Sol. Energy* **2019**, *193*, 275–282. [[CrossRef](#)]
21. Liang, G.-X.; Luo, Y.-D.; Chen, S.; Tang, R.; Zheng, Z.-H.; Li, X.-J.; Liu, X.-S.; Liu, Y.-K.; Li, Y.-F.; Chen, X.-Y.; et al. Sputtered and Selenized  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cells with Open-Circuit Voltage Exceeding 500 mV. *Nano Energy* **2020**, *73*, 104806. [[CrossRef](#)]
22. Alamri, S.N. The Growth of CdTe Thin Film by Close Space Sublimation System. *Phys. Status Solidi A* **2003**, *200*, 352–360. [[CrossRef](#)]
23. Guo, L.; Zhang, B.; Qin, Y.; Li, D.; Li, L.; Qian, X.; Yan, F. Tunable Quasi-One-Dimensional Ribbon Enhanced Light Absorption in  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cells Grown by Close-Space Sublimation. *Sol. RRL* **2018**, *2*, 1800128. [[CrossRef](#)]
24. Tao, R.; Tan, T.; Zhang, H.; Meng, Q.; Zha, G.  $\text{Sb}_2\text{Se}_3$  Solar Cells Fabricated via Close-Space Sublimation. *J. Vac. Sci. Technol. B* **2021**, *39*, 052203. [[CrossRef](#)]
25. Li, Z.; Liang, X.; Li, G.; Liu, H.; Zhang, H.; Guo, J.; Chen, J.; Shen, K.; San, X.; Yu, W.; et al. 9.2%-Efficient Core-Shell Structured Antimony Selenide Nanorod Array Solar Cells. *Nat. Commun.* **2019**, *10*, 125. [[CrossRef](#)] [[PubMed](#)]
26. Guo, H.; Zhao, C.; Xing, Y.; Tian, H.; Yan, D.; Zhang, S.; Jia, X.; Qiu, J.; Yuan, N.; Ding, J. High-Efficiency  $\text{Sb}_2\text{Se}_3$  Solar Cells Modified by Potassium Hydroxide. *J. Phys. Chem. Lett.* **2021**, *12*, 12352–12359. [[CrossRef](#)]
27. Chen, C.; Li, K.; Chen, S.; Wang, L.; Lu, S.; Liu, Y.; Li, D.; Song, H.; Tang, J. Efficiency Improvement of  $\text{Sb}_2\text{Se}_3$  Solar Cells via Grain Boundary Inversion. *ACS Energy Lett.* **2018**, *3*, 2335–2341. [[CrossRef](#)]
28. Wen, X.; Chen, C.; Lu, S.; Li, K.; Kondrotas, R.; Zhao, Y.; Chen, W.; Gao, L.; Wang, C.; Zhang, J.; et al. Vapor Transport Deposition of Antimony Selenide Thin Film Solar Cells with 7.6% Efficiency. *Nat. Commun.* **2018**, *9*, 2179. [[CrossRef](#)]
29. Duan, Z.; Liang, X.; Feng, Y.; Ma, H.; Liang, B.; Wang, Y.; Luo, S.; Wang, S.; Schropp, R.E.I.; Mai, Y.; et al.  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cells Exceeding 10% Power Conversion Efficiency Enabled by Injection Vapor Deposition Technology. *Adv. Mater.* **2022**, *34*, 2202969. [[CrossRef](#)]
30. Yang, K.; Li, B.; Zeng, G.  $\text{Sb}_2\text{Se}_3$  Thin Film Solar Cells Prepared by Pulsed Laser Deposition. *J. Alloys Compd.* **2020**, *821*, 153505. [[CrossRef](#)]
31. Ashfold, M.N.R.; Claeysens, F.; Fuge, G.M.; Henley, S.J. Pulsed Laser Ablation and Deposition of Thin Films. *Chem. Soc. Rev.* **2004**, *33*, 23. [[CrossRef](#)]
32. Pattini, F.; Rampino, S.; Mezzadri, F.; Calestani, D.; Spaggiari, G.; Sidoli, M.; Delmonte, D.; Sala, A.; Gilioli, E.; Mazzer, M. Role of the Substrates in the Ribbon Orientation of  $\text{Sb}_2\text{Se}_3$  Films Grown by Low-Temperature Pulsed Electron Deposition. *Sol. Energy Mater. Sol. Cells* **2020**, *218*, 110724. [[CrossRef](#)]
33. Pattini, F.; Bronzoni, M.; Mezzadri, F.; Bissoli, F.; Gilioli, E.; Rampino, S. Dynamics of Evaporation from  $\text{CuGaSe}_2$  Targets in Pulsed Electron Deposition Technique. *J. Phys. D Appl. Phys.* **2013**, *46*, 245101. [[CrossRef](#)]

34. Shen, K.; Zhang, Y.; Wang, X.; Ou, C.; Guo, F.; Zhu, H.; Liu, C.; Gao, Y.; Schropp, R.E.I.; Li, Z.; et al. Efficient and Stable Planar n-i-p Sb<sub>2</sub>Se<sub>3</sub> Solar Cells Enabled by Oriented 1D Trigonal Selenium Structures. *Adv. Sci.* **2020**, *7*, 2001013. [[CrossRef](#)]
35. Bérubé, L.P.; L'Espérance, G. A Quantitative Method of Determining the Degree of Texture of Zinc Electrodeposits. *J. Electrochem. Soc.* **1989**, *136*, 2314–2315. [[CrossRef](#)]
36. Krautmann, R.; Spalatu, N.; Gunder, R.; Abou-Ras, D.; Unold, T.; Schorr, S.; Krunks, M.; Oja Acik, I. Analysis of Grain Orientation and Defects in Sb<sub>2</sub>Se<sub>3</sub> Solar Cells Fabricated by Close-Spaced Sublimation. *Sol. Energy* **2021**, *225*, 494–500. [[CrossRef](#)]
37. Spalatu, N.; Krautmann, R.; Katerski, A.; Karber, E.; Josepson, R.; Hiie, J.; Acik, I.O.; Krunks, M. Screening and Optimization of Processing Temperature for Sb<sub>2</sub>Se<sub>3</sub> Thin Film Growth Protocol: Interrelation between Grain Structure, Interface Intermixing and Solar Cell Performance. *Sol. Energy Mater. Sol. Cells* **2021**, *225*, 111045. [[CrossRef](#)]
38. Zhou, J.; Meng, D.; Yang, T.; Zhang, X.; Tang, Z.; Cao, Y.; Ni, J.; Zhang, J.; Hu, Z.; Pang, J. Enhanced Charge Carrier Transport via Efficient Grain Conduction Mode for Sb<sub>2</sub>Se<sub>3</sub> Solar Cell Applications. *Appl. Surf. Sci.* **2022**, *591*, 153169. [[CrossRef](#)]
39. Liang, X.; Li, Z.; San, X.; Liu, T.; Liu, Y.; Shen, K.; Wang, S.; Schropp, R.E.I.; Mai, Y. Nanoeptaxy Growth of Sb<sub>2</sub>Se<sub>3</sub> Nanorod Arrays on Mixed-Oriented Transparent Conducting Oxide-Coated Glass for Efficient and Quasiomnidirectional Solar Cells. *Sol. RRL* **2022**, *6*, 2100869. [[CrossRef](#)]
40. Wang, W.; Cao, Z.; Zuo, X.; Wu, L.; Luo, J.; Zhang, Y. Double Interface Modification Promotes Efficient Sb<sub>2</sub>Se<sub>3</sub> Solar Cell by Tailoring Band Alignment and Light Harvest. *J. Energy Chem.* **2022**, *70*, 191–200. [[CrossRef](#)]
41. Lin, W.-W.; Wang, N.-W.; Lan, Z.-Y.; Fu, Z.; Huang, Z.-P.; Lin, L.-M.; Ye, Q.-Y.; Chen, S.-Y.; Chen, G.-L. Construction of CdS/Sb<sub>2</sub>Se<sub>3</sub> Planar Heterojunction by Full Vapor Transport Deposition. *Vacuum* **2022**, *206*, 111544. [[CrossRef](#)]
42. Tang, R.; Zheng, Z.-H.; Su, Z.-H.; Li, X.-J.; Wei, Y.-D.; Zhang, X.-H.; Fu, Y.-Q.; Luo, J.-T.; Fan, P.; Liang, G.-X. Highly Efficient and Stable Planar Heterojunction Solar Cell Based on Sputtered and Post-Selenized Sb<sub>2</sub>Se<sub>3</sub> Thin Film. *Nano Energy* **2019**, *64*, 103929. [[CrossRef](#)]
43. Park, S.-N.; Kim, S.-Y.; Lee, S.-J.; Sung, S.-J.; Yang, K.-J.; Kang, J.-K.; Kim, D.-H. Controlled Synthesis of (*Hk* 1) Preferentially Oriented Sb<sub>2</sub>Se<sub>3</sub> Rod Arrays by Co-Evaporation for Photovoltaic Applications. *J. Mater. Chem. A* **2019**, *7*, 25900–25907. [[CrossRef](#)]
44. Liu, C.; Pan, Z.; Shen, K.; Zheng, J.; Liang, X.; Zhu, H.; Guo, F.; Li, Z.; Schropp, R.E.I.; Mai, Y. Interpenetrating Structure for Efficient Sb<sub>2</sub>Se<sub>3</sub> Nanorod Array Solar Cells Loaded with CuInSe<sub>2</sub> QDs Sensitizer. *J. Energy Chem.* **2022**, *68*, 521–528. [[CrossRef](#)]
45. Guo, C.; Liang, X.; Liu, T.; Liu, Y.; Yang, L.; Lai, W.; Schropp, R.E.I.; Song, D.; Mai, Y.; Li, Z. 1D/3D Alloying Induced Phase Transition in Light Absorbers for Highly Efficient Sb<sub>2</sub>Se<sub>3</sub> Solar Cells. *Sol. RRL* **2020**, *4*, 2000054. [[CrossRef](#)]
46. Fan, P.; Chen, G.-J.; Chen, S.; Zheng, Z.-H.; Azam, M.; Ahmad, N.; Su, Z.-H.; Liang, G.-X.; Zhang, X.-H.; Chen, Z.-G. Quasi-Vertically Oriented Sb<sub>2</sub>Se<sub>3</sub> Thin-Film Solar Cells with Open-Circuit Voltage Exceeding 500 mV Prepared via Close-Space Sublimation and Selenization. *ACS Appl. Mater. Interfaces* **2021**, *13*, 46671–46680. [[CrossRef](#)]
47. Amin, A.; Duan, X.; Wall, J.; Khawaja, K.A.; Xiang, W.; Li, L.; Yan, F. Heterostructured CdS Buffer Layer for Sb<sub>2</sub>Se<sub>3</sub> Thin Film Solar Cell. *Sol. RRL* **2023**, *7*, 2300417. [[CrossRef](#)]
48. Pasini, S.; Spoltore, D.; Parisini, A.; Foti, G.; Marchionna, S.; Vantaggio, S.; Fornari, R.; Bosio, A. Sb<sub>2</sub>Se<sub>3</sub> Polycrystalline Thin Films Grown on Different Window Layers. *Coatings* **2023**, *13*, 338. [[CrossRef](#)]
49. Kim, J.; Ji, S.; Jang, Y.; Jeong, G.; Choi, J.; Kim, D.; Nam, S.-W.; Shin, B. Importance of Fine Control of Se Flux for Improving Performances of Sb<sub>2</sub>Se<sub>3</sub> Solar Cells Prepared by Vapor Transport Deposition. *Sol. RRL* **2021**, *5*, 2100327. [[CrossRef](#)]
50. Dong, S.; Sun, L.; Yue, F. Influence of Selenium Growth Condition on the Photovoltaic Conversion Efficiency of Sb<sub>2</sub>Se<sub>3</sub> as the Solar Cell Absorption Layer. *J. Mater. Sci Mater. Electron.* **2022**, *33*, 10335–10342. [[CrossRef](#)]
51. Zi, W.; Mu, F.; Lu, X.; Liu, Z.; Pang, X.; Yu, Z.; Li, Y.; Zhao, Z.; Lei, B.; Cheng, N.; et al. Sputtering Al<sub>2</sub>O<sub>3</sub> as an Effective Interface Layer to Improve Open-Circuit Voltage and Device Performance of Sb<sub>2</sub>Se<sub>3</sub> Thin-Film Solar Cells. *Mater. Sci. Semicond. Process.* **2023**, *153*, 107185. [[CrossRef](#)]
52. Kumar, V.; Artagiani, E.; Punathil, P.; Bertinello, M.; Meneghini, M.; Piccinelli, F.; Romeo, A. Analysis of Se Co-Evaporation and Post-Selenization for Sb<sub>2</sub>Se<sub>3</sub>-Based Solar Cells. *ACS Appl. Energy Mater.* **2021**, *4*, 12479–12486. [[CrossRef](#)]
53. Guo, H.; Chen, Z.; Wang, X.; Cang, Q.; Jia, X.; Ma, C.; Yuan, N.; Ding, J. Enhancement in the Efficiency of Sb<sub>2</sub>Se<sub>3</sub> Thin-Film Solar Cells by Increasing Carrier Concentration and Inducing Columnar Growth of the Grains. *Sol. RRL* **2019**, *3*, 1800224. [[CrossRef](#)]
54. Liu, Y.; Liu, X.; Zhuang, Y.; Li, E.; Zhang, S.; Liu, J.; Cheng, K.; Du, Z. Nanorod Array-Induced Growth of High-Quality Sb<sub>2</sub>Se<sub>3</sub> Absorber Layers for Efficient Planar Solar Cells. *J. Alloys Compd.* **2023**, *949*, 169729. [[CrossRef](#)]
55. Wen, X.; Lu, Z.; Yang, X.; Chen, C.; Washington, M.A.; Wang, G.-C.; Tang, J.; Zhao, Q.; Lu, T.-M. Vertically Aligned One-Dimensional Crystal-Structured Sb<sub>2</sub>Se<sub>3</sub> for High-Efficiency Flexible Solar Cells via Regulating Selenization Kinetics. *ACS Appl. Mater. Interfaces* **2023**, *15*, 22251–22262. [[CrossRef](#)]
56. Rijal, S.; Li, D.-B.; Awni, R.A.; Bista, S.S.; Song, Z.; Yan, Y. Influence of Post-Selenization Temperature on the Performance of Substrate-Type Sb<sub>2</sub>Se<sub>3</sub> Solar Cells. *ACS Appl. Energy Mater.* **2021**, *4*, 4313–4318. [[CrossRef](#)]
57. Yuan, C.; Zhang, L.; Liu, W.; Zhu, C. Rapid Thermal Process to Fabricate Sb<sub>2</sub>Se<sub>3</sub> Thin Film for Solar Cell Application. *Sol. Energy* **2016**, *137*, 256–260. [[CrossRef](#)]
58. Caño, I.; Vidal-Fuentes, P.; Calvo-Barrio, L.; Alcobé, X.; Asensi, J.M.; Giraldo, S.; Sánchez, Y.; Jehl, Z.; Placidi, M.; Puigdollers, J.; et al. Does Sb<sub>2</sub>Se<sub>3</sub> Admit Nonstoichiometric Conditions? How Modifying the Overall Se Content Affects the Structural, Optical, and Optoelectronic Properties of Sb<sub>2</sub>Se<sub>3</sub> Thin Films. *ACS Appl. Mater. Interfaces* **2022**, *14*, 11222–11234. [[CrossRef](#)] [[PubMed](#)]
59. Yang, Y.; Guo, T.; Wang, D.; Xiong, X.; Li, B. Preparation and Characterization of Pulsed Laser Deposited CdSe Window Layer for Sb<sub>2</sub>Se<sub>3</sub> Thin Film Solar Cell. *J. Mater. Sci Mater. Electron.* **2020**, *31*, 13947–13956. [[CrossRef](#)]

60. Shiel, H.; Hutter, O.S.; Phillips, L.J.; Swallow, J.E.N.; Jones, L.A.H.; Featherstone, T.J.; Smiles, M.J.; Thakur, P.K.; Lee, T.-L.; Dhanak, V.R.; et al. Natural Band Alignments and Band Offsets of  $\text{Sb}_2\text{Se}_3$  Solar Cells. *ACS Appl. Energy Mater.* **2020**, *3*, 11617–11626. [[CrossRef](#)]
61. Lu, S.; Ding, H.; Hu, J.; Liu, Y.; Zhu, J.; Kondrotas, R.; Chen, C.; Tang, J. In Situ Investigation of Interfacial Properties of  $\text{Sb}_2\text{Se}_3$  Heterojunctions. *Appl. Phys. Lett.* **2020**, *116*, 241602. [[CrossRef](#)]
62. Mavlonov, A.; Razykov, T.; Raziq, F.; Gan, J.; Chantana, J.; Kawano, Y.; Nishimura, T.; Wei, H.; Zakutayev, A.; Minemoto, T.; et al. A Review of  $\text{Sb}_2\text{Se}_3$  Photovoltaic Absorber Materials and Thin-Film Solar Cells. *Sol. Energy* **2020**, *201*, 227–246. [[CrossRef](#)]
63. Rahman, F.; Alam Moon, M.; Hossain, M.K.; Ali, H.; Haque, D.; Kuddus, A.; Hossain, J.; Ismail, A.B. Concurrent Investigation of Antimony Chalcogenide ( $\text{Sb}_2\text{Se}_3$  and  $\text{Sb}_2\text{S}_3$ )-Based Solar Cells with a Potential  $\text{WS}_2$  Electron Transport Layer. *Heliyon* **2022**, *8*, e12034. [[CrossRef](#)] [[PubMed](#)]
64. Ayala-Mató, F.; Vigil-Galán, O.; Seuret-Jiménez, D.; Courel, M.; Fernández, S. Evaluation of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$  as Electron Transport Layer in Superstrate and Inverted Configurations of  $\text{Sb}_2\text{Se}_3$  Solar Cells with n-i-p Structure. *Semicond. Sci. Technol.* **2021**, *36*, 015016. [[CrossRef](#)]
65. Salem, M.S.; Shaker, A.; Abouelatta, M.; Alanazi, A.; Al-Dhlan, K.A.; Almurayziq, T.S. Numerical Analysis of Hole Transport Layer-Free Antimony Selenide Solar Cells: Possible Routes for Efficiency Promotion. *Opt. Mater.* **2022**, *129*, 112473. [[CrossRef](#)]
66. Kumari, R.; Mamta, M.; Kumar, R.; Singh, Y.; Singh, V.N. 24% Efficient, Simple  $\text{ZnSe}/\text{Sb}_2\text{Se}_3$  Heterojunction Solar Cell: An Analysis of PV Characteristics and Defects. *ACS Omega* **2023**, *8*, 1632–1642. [[CrossRef](#)]
67. Luo, Y.; Chen, G.; Chen, S.; Ahmad, N.; Azam, M.; Zheng, Z.; Su, Z.; Cathelinaud, M.; Ma, H.; Chen, Z.; et al. Carrier Transport Enhancement Mechanism in Highly Efficient Antimony Selenide Thin-Film Solar Cell. *Adv. Funct. Mater.* **2023**, *33*, 2213941. [[CrossRef](#)]
68. Cai, H.; Cao, R.; Gao, J.; Qian, C.; Che, B.; Tang, R.; Zhu, C.; Chen, T. Interfacial Engineering towards Enhanced Photovoltaic Performance of  $\text{Sb}_2\text{Se}_3$  Solar Cell. *Adv. Funct. Mater.* **2022**, *32*, 2208243. [[CrossRef](#)]
69. Cheng, J.; Zhang, Z.; Zhao, M.; Guan, Y.; Chen, X.; Meng, X.; Tang, H.; Li, L.; Wang, S. High-Efficiency  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cells Based on  $\text{Cd}(\text{S},\text{O})$  Buffer Layers Prepared via Spin-Coating. *Mater. Chem. Phys.* **2023**, *303*, 127794. [[CrossRef](#)]
70. Liu, Y.; Li, B.; Liang, X.; Liu, T.; Wang, S.; Li, Z. Reactively Sputtered  $\text{CdS}:\text{O}$  Buffer Layers for Substrate  $\text{Sb}_2\text{Se}_3$  Solar Cells. *J. Alloys Compd.* **2023**, *932*, 167313. [[CrossRef](#)]
71. Guo, L.; Zhang, B.; Ranjit, S.; Wall, J.; Saurav, S.; Hauser, A.J.; Xing, G.; Li, L.; Qian, X.; Yan, F. Interface Engineering via Sputtered Oxygenated  $\text{CdS}:\text{O}$  Window Layer for Highly Efficient  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cells with Efficiency Above 7%. *Sol. RRL* **2019**, *3*, 1900225. [[CrossRef](#)]
72. Mao, X.; Wang, C.; Bian, M.; Wan, L.; Yang, X.; Zhou, R. The Design of  $\text{SnO}_2$ -Dominated Electron Transport Layer for High-Efficiency  $\text{Sb}_2(\text{S},\text{Se})_3$  Solar Cells. *Phys. Status Solidi A* **2022**, *219*, 2200576. [[CrossRef](#)]
73. Li, G.; Li, Z.; Liang, X.; Guo, C.; Shen, K.; Mai, Y. Improvement in  $\text{Sb}_2\text{Se}_3$  Solar Cell Efficiency through Band Alignment Engineering at the Buffer/Absorber Interface. *ACS Appl. Mater. Interfaces* **2019**, *11*, 828–834. [[CrossRef](#)]
74. Zhou, J.; Zhang, X.; Chen, H.; Tang, Z.; Meng, D.; Chi, K.; Cai, Y.; Song, G.; Cao, Y.; Hu, Z. Dual-Function of  $\text{CdCl}_2$  Treated  $\text{SnO}_2$  in  $\text{Sb}_2\text{Se}_3$  Solar Cells. *Appl. Surf. Sci.* **2020**, *534*, 147632. [[CrossRef](#)]
75. Wen, S.; Yin, X.; Zhang, C.; Guo, Y.; Liu, J.; Wang, E.; Zheng, C.; Que, W.; Liu, H.; Liu, W. Achievable Efficiency Improvement of  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cells through Interface Engineering. *Mater. Lett.* **2021**, *283*, 128770. [[CrossRef](#)]
76. Chen, Z.; Guo, H.; Ma, C.; Wang, X.; Jia, X.; Yuan, N.; Ding, J. Efficiency Improvement of  $\text{Sb}_2\text{Se}_3$  Solar Cells Based on La-Doped  $\text{SnO}_2$  Buffer Layer. *Sol. Energy* **2019**, *187*, 404–410. [[CrossRef](#)]
77. Wang, Y.; Tang, R.; Huang, L.; Qian, C.; Lian, W.; Zhu, C.; Chen, T. Post-Treatment of  $\text{TiO}_2$  Film Enables High-Quality  $\text{Sb}_2\text{Se}_3$  Film Deposition for Solar Cell Applications. *ACS Appl. Mater. Interfaces* **2022**, *14*, 33181–33190. [[CrossRef](#)]
78. Wang, X.; Guo, H.; Chen, Z.; Ma, C.; Fang, X.; Jia, X.; Yuan, N.; Ding, J. Enhancement of  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cell Photoelectric Properties by Addition of Interlayer  $\text{CeO}_2$ . *Sol. Energy* **2019**, *188*, 218–223. [[CrossRef](#)]
79. Zhang, J.; Guo, H.; Jia, X.; Ning, H.; Ma, C.; Wang, X.; Qiu, J.; Yuan, N.; Ding, J. Improving the Performance of  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cells Using n-Type  $\text{MoO}_3$  as the Back Contact Layer. *Sol. Energy* **2021**, *214*, 231–238. [[CrossRef](#)]
80. Wang, W.; Yao, L.; Dong, J.; Wu, L.; Cao, Z.; Hui, L.; Chen, G.; Luo, J.; Zhang, Y. Interface Modification Uncovers the Potential Application of  $\text{SnO}_2/\text{TiO}_2$  Double Electron Transport Layer in Efficient Cadmium-Free  $\text{Sb}_2\text{Se}_3$  Devices. *Adv. Mater. Interfaces* **2022**, *9*, 2102464. [[CrossRef](#)]
81. Luo, Y.-D.; Chen, M.; Tang, R.; Azam, M.; Chen, S.; Zheng, Z.-H.; Su, Z.-H.; Fan, P.; Ma, H.-L.; Liang, G.-X.; et al. Energy Band Alignment for Cd-Free Antimony Triselenide Substrate Structured Solar Cells by Co-Sputtering  $\text{ZnSnO}$  Buffer Layer. *Sol. Energy Mater. Sol. Cells* **2022**, *240*, 111721. [[CrossRef](#)]
82. Dong, Y.; Huang, L.; Wang, H.; Peng, X.; Wang, Y.; Tang, R.; Zhu, C.; Chen, T. Zinc Chloride-Treated Indium Sulfide as Buffer Layer for Cd-Free Antimony Selenide Solar Cells. *Sol. RRL* **2023**, *7*, 2300440. [[CrossRef](#)]
83. Cheng, C.-H.; Li, M.; Song, H.-Q.; Li, W.-H.; Leng, J.; Tian, W.; Cui, R.; Zhao, C.; Jin, S.; Liu, W.; et al. Enhanced Performance of the  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cell by Organic Molecule-Induced Crystallization and Suppression of the Interface Recombination. *ACS Appl. Energy Mater.* **2021**, *4*, 5079–5085. [[CrossRef](#)]
84. Rovira, D.; Ros, E.; Tom, T.; Jiménez, M.; Miguel Asensi, J.; Voz, C.; López-Vidrier, J.; Puigdollers, J.; Bertomeu, J.; Saucedo, E. Polymeric Interlayer in CdS-Free Electron-Selective Contact for  $\text{Sb}_2\text{Se}_3$  Thin-Film Solar Cells. *Int. J. Mol. Sci.* **2023**, *24*, 3088. [[CrossRef](#)] [[PubMed](#)]

85. Li, K.; Wang, S.; Chen, C.; Kondrotas, R.; Hu, M.; Lu, S.; Wang, C.; Chen, W.; Tang, J. 7.5% n-i-p Sb<sub>2</sub>Se<sub>3</sub> Solar Cells with CuSCN as a Hole-Transport Layer. *J. Mater. Chem. A* **2019**, *7*, 9665–9672. [[CrossRef](#)]
86. Liu, C.; Shen, K.; Lin, D.; Cao, Y.; Qiu, S.; Zheng, J.; Bao, F.; Gao, Y.; Zhu, H.; Li, Z.; et al. Back Contact Interfacial Modification in Highly-Efficient All-Inorganic Planar n-i-p Sb<sub>2</sub>Se<sub>3</sub> Solar Cells. *ACS Appl. Mater. Interfaces* **2020**, *12*, 38397–38405. [[CrossRef](#)]
87. Zhang, J.; Kondrotas, R.; Lu, S.; Wang, C.; Chen, C.; Tang, J. Alternative Back Contacts for Sb<sub>2</sub>Se<sub>3</sub> Solar Cells. *Sol. Energy* **2019**, *182*, 96–101. [[CrossRef](#)]
88. Ma, Y.; Yin, Y.; Li, G.; Lian, W.; Zhang, J.; Tang, R.; Ju, H.; Chen, T. Aqueous Solution Processed MoS<sub>3</sub> as an Eco-Friendly Hole-Transport Layer for All-Inorganic Sb<sub>2</sub>Se<sub>3</sub> Solar Cells. *Chem. Commun.* **2020**, *56*, 15173–15176. [[CrossRef](#)]
89. Lin, J.; Chen, G.; Ahmad, N.; Ishaq, M.; Chen, S.; Su, Z.; Fan, P.; Zhang, X.; Zhang, Y.; Liang, G. Back Contact Interfacial Modification Mechanism in Highly-Efficient Antimony Selenide Thin-Film Solar Cells. *J. Energy Chem.* **2023**, *80*, 256–264. [[CrossRef](#)]
90. Cang, Q.; Guo, H.; Jia, X.; Ning, H.; Ma, C.; Zhang, J.; Yuan, N.; Ding, J. Enhancement in the Efficiency of Sb<sub>2</sub>Se<sub>3</sub> Solar Cells by Adding Low Lattice Mismatch CuSbSe<sub>2</sub> Hole Transport Layer. *Sol. Energy* **2020**, *199*, 19–25. [[CrossRef](#)]
91. Liang, X.; Feng, Y.; Dang, W.; Huang, H.; Wang, X.; Guo, Y.; Shen, K.; Schropp, R.E.I.; Li, Z.; Mai, Y. High-Efficiency Flexible Sb<sub>2</sub>Se<sub>3</sub> Solar Cells by Back Interface and Absorber Bulk Deep-Level Trap Engineering. *ACS Energy Lett.* **2023**, *8*, 213–221. [[CrossRef](#)]
92. Hutter, O.S.; Phillips, L.J.; Durose, K.; Major, J.D. 6.6% Efficient Antimony Selenide Solar Cells Using Grain Structure Control and an Organic Contact Layer. *Sol. Energy Mater. Sol. Cells* **2018**, *188*, 177–181. [[CrossRef](#)]
93. Don, C.H.; Shalvey, T.P.; Smiles, M.J.; Thomas, L.; Phillips, L.J.; Hobson, T.D.C.; Finch, H.; Jones, L.A.H.; Swallow, J.E.N.; Fleck, N.; et al. Multi-Phase Sputtered TiO<sub>2</sub>-Induced Current-Voltage Distortion in Sb<sub>2</sub>Se<sub>3</sub> Solar Cells. *Adv. Mater. Interfaces* **2023**, *10*, 2300238. [[CrossRef](#)]
94. Cao, Z.; Wang, W.; Dong, J.; Lou, L.; Liu, H.; Wang, Z.; Luo, J.; Liu, Y.; Dai, Y.; Li, D.; et al. Oxygen Content Modulation toward Highly Efficient Sb<sub>2</sub>Se<sub>3</sub> Solar Cells. *ACS Appl. Mater. Interfaces* **2022**, *14*, 55691–55699. [[CrossRef](#)]
95. Cao, Y.; Zhu, X.; Chen, H.; Zhang, X.; Zhou, J.; Hu, Z.; Pang, J. Towards High Efficiency Inverted Sb<sub>2</sub>Se<sub>3</sub> Thin Film Solar Cells. *Sol. Energy Mater. Sol. Cells* **2019**, *200*, 109945. [[CrossRef](#)]
96. Sunny, A.; Ahmed, S.R.A. Numerical Simulation and Performance Evaluation of Highly Efficient Sb<sub>2</sub>Se<sub>3</sub> Solar Cell with Tin Sulfide as Hole Transport Layer. *Phys. Status Solidi B* **2021**, *258*, 2000630. [[CrossRef](#)]
97. Campbell, S.; Phillips, L.J.; Major, J.D.; Hutter, O.S.; Joyce, R.; Qu, Y.; Beattie, N.S.; Zoppi, G.; Barrioz, V. Routes to Increase Performance for Antimony Selenide Solar Cells Using Inorganic Hole Transport Layers. *Front. Chem.* **2022**, *10*, 954588. [[CrossRef](#)]
98. Pasini, S.; Spoltore, D.; Parisini, A.; Marchionna, S.; Fornasini, L.; Bersani, D.; Fornari, R.; Bosio, A. Innovative Back-Contact for Sb<sub>2</sub>Se<sub>3</sub>-Based Thin Film Solar Cells. *Sol. Energy* **2023**, *249*, 414–423. [[CrossRef](#)]
99. Li, Y.; Zhou, Y.; Luo, J.; Chen, W.; Yang, B.; Wen, X.; Lu, S.; Chen, C.; Zeng, K.; Song, H.; et al. The Effect of Sodium on Antimony Selenide Thin Film Solar Cells. *RSC Adv.* **2016**, *6*, 87288–87293. [[CrossRef](#)]
100. Li, W.-H.; Li, M.; Hu, Y.-J.; Cheng, C.-H.; Kan, Z.-M.; Yu, D.; Leng, J.; Jin, S.; Cong, S. Enhanced Performance of Antimony Selenide Thin Film Solar Cell Using PbI<sub>2</sub> as a Dopant. *Appl. Phys. Lett.* **2021**, *118*, 093903. [[CrossRef](#)]
101. Huang, M.; Lu, S.; Li, K.; Lu, Y.; Chen, C.; Tang, J.; Chen, S. P-Type Antimony Selenide via Lead Doping. *Sol. RRL* **2022**, *6*, 2100730. [[CrossRef](#)]
102. Ma, Y.; Tang, B.; Lian, W.; Wu, C.; Wang, X.; Ju, H.; Zhu, C.; Fan, F.; Chen, T. Efficient Defect Passivation of Sb<sub>2</sub>Se<sub>3</sub> Film by Tellurium Doping for High Performance Solar Cells. *J. Mater. Chem. A* **2020**, *8*, 6510–6516. [[CrossRef](#)]
103. Tiwari, K.J.; Neuschitzer, M.; Espindola, M.; Sanchez, Y.; Vidal, P.; Saucedo, E.; Malar, P. Tailoring Doping of Efficient Sb<sub>2</sub>Se<sub>3</sub> Solar Cells in Substrate Configuration by Low Temperature Post Deposition Selenization Process. In Proceedings of the 2018 IEEE 7th World Conference on Photovoltaic Energy Conversion (WCPEC) (A Joint Conference of 45th IEEE PVSC, 28th PVSEC & 34th EU PVSEC), Waikoloa Village, HI, USA, 10–15 June 2018; IEEE: Waikoloa Village, HI, USA, 2018; pp. 1858–1860. [[CrossRef](#)]
104. Spaggiari, G.; Bersani, D.; Calestani, D.; Gilioli, E.; Gombia, E.; Mezzadri, F.; Casappa, M.; Pattini, F.; Trevisi, G.; Rampino, S. Exploring Cu-Doping for Performance Improvement in Sb<sub>2</sub>Se<sub>3</sub> Photovoltaic Solar Cells. *Int. J. Mol. Sci.* **2022**, *23*, 15529. [[CrossRef](#)] [[PubMed](#)]
105. Li, Y.; Zhou, Y.; Zhu, Y.; Chen, C.; Luo, J.; Ma, J.; Yang, B.; Wang, X.; Xia, Z.; Tang, J. Characterization of Mg and Fe Doped Sb<sub>2</sub>Se<sub>3</sub> Thin Films for Photovoltaic Application. *Appl. Phys. Lett.* **2016**, *109*, 232104. [[CrossRef](#)]
106. Liu, X.; Xiao, X.; Yang, Y.; Xue, D.-J.; Li, D.-B.; Chen, C.; Lu, S.; Gao, L.; He, Y.; Beard, M.C.; et al. Enhanced Sb<sub>2</sub>Se<sub>3</sub> Solar Cell Performance through Theory-Guided Defect Control: Enhanced Sb<sub>2</sub>Se<sub>3</sub> Solar Cell Performance. *Prog. Photovolt. Res. Appl.* **2017**, *25*, 861–870. [[CrossRef](#)]
107. Hobson, T.D.C.; Phillips, L.J.; Hutter, O.S.; Shiel, H.; Swallow, J.E.N.; Savory, C.N.; Nayak, P.K.; Mariotti, S.; Das, B.; Bowen, L.; et al. Isotype Heterojunction Solar Cells Using N-Type Sb<sub>2</sub>Se<sub>3</sub> Thin Films. *Chem. Mater.* **2020**, *32*, 2621–2630. [[CrossRef](#)]
108. Hobson, T.D.C.; Shiel, H.; Savory, C.N.; Swallow, J.E.N.; Jones, L.A.H.; Featherstone, T.J.; Smiles, M.J.; Thakur, P.K.; Lee, T.-L.; Das, B.; et al. P-Type Conductivity in Sn-Doped Sb<sub>2</sub>Se<sub>3</sub>. *J. Phys. Energy* **2022**, *4*, 045006. [[CrossRef](#)]
109. Chen, S.; Qiao, X.; Zheng, Z.; Cathelinaud, M.; Ma, H.; Fan, X.; Zhang, X. Enhanced Electrical Conductivity and Photoconductive Properties of Sn-Doped Sb<sub>2</sub>Se<sub>3</sub> Crystals. *J. Mater. Chem. C* **2018**, *6*, 6465–6470. [[CrossRef](#)]
110. Costa, M.B.; De Souza Lucas, F.W.; Mascaro, L.H. Electrodeposition of Fe-Doped Sb<sub>2</sub>Se<sub>3</sub> Thin Films for Photoelectrochemical Applications and Study of the Doping Effects on Their Properties. *J. Solid State Electrochem.* **2018**, *22*, 1557–1562. [[CrossRef](#)]

111. Zhou, H.; Feng, M.; Gong, X.; Zhang, D.; Zhou, Y.; Chen, S. Gradient Doping of Sulfur in Sb<sub>2</sub>Se<sub>3</sub> Nanowire Arrays as Photoelectrochemical Photocathode with a 2% Half-Cell Solar-to-Hydrogen Conversion Efficiency. *Appl. Phys. Lett.* **2020**, *116*, 113902. [[CrossRef](#)]
112. Baghbanzadeh-Dezfuli, B.; Jamali-Sheini, F.; Cheraghizade, M. Electrochemical Synthesis of S-Doped Sb<sub>2</sub>Se<sub>3</sub> Nanostructures and Photo-Switching Behaviour. *Opt. Quantum Electron.* **2023**, *55*, 4. [[CrossRef](#)]
113. Gautam, S.; Thakur, A.; Tripathi, S.K.; Goyal, N. Effect of Silver Doping on the Electrical Properties of A- Sb<sub>2</sub>Se<sub>3</sub>. *J. Non-Cryst. Solids* **2007**, *353*, 1315–1321. [[CrossRef](#)]
114. Wu, W.; Li, Y.; Liang, L.; Hao, Q.; Zhang, J.; Liu, H.; Liu, C. Enhanced Broadband Responsivity of Ni-Doped Sb<sub>2</sub>Se<sub>3</sub> Nanorod Photodetector. *J. Phys. Chem. C* **2019**, *123*, 14781–14789. [[CrossRef](#)]
115. Li, J.; Wang, B.; Liu, F.; Yang, J.; Li, J.; Liu, J.; Jia, M.; Lai, Y.; Liu, Y. Preparation and Characterization of Bi-Doped Antimony Selenide Thin Films by Electrodeposition. *Electrochim. Acta* **2011**, *56*, 8597–8602. [[CrossRef](#)]
116. Chen, S.; Luo, P.; Ren, D.-L.; Duan, C.-Y.; Ma, X.-F.; Su, Z.-H.; Zheng, Z.-H.; Fan, P.; Liang, G.-X.; Tang, R. An Effective Engineering with Simultaneous Carrier Density Enhancement and Interface Optimization Enables Efficient Sb<sub>2</sub>Se<sub>3</sub> Solar Cells. *Appl. Surf. Sci.* **2023**, *619*, 156783. [[CrossRef](#)]
117. Chen, G.; Li, X.; Abbas, M.; Fu, C.; Su, Z.; Tang, R.; Chen, S.; Fan, P.; Liang, G. Tellurium Doping Inducing Defect Passivation for Highly Effective Antimony Selenide Thin Film Solar Cell. *Nanomaterials* **2023**, *13*, 1240. [[CrossRef](#)] [[PubMed](#)]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.