

Review

Beyond CdS: Buffer Layers, Front Interfaces and Junction Engineering in p-Type Thin-Film Solar Cells

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Abstract

Cadmium sulfide has been widely used as a conventional n-type window /buffer layer or heterojunction partner in several p-type thin-film solar cells, including CdTe/CdSeTe-, chalcopyrite-, kesterite-, antimony chalcogenide-, tin sulfide- and iron pyrite-based devices. Its success is related to its ability to form suitable heterojunctions, partially passivate absorber surfaces and provide favorable electronic selectivity. However, the parasitic absorption associated with the relatively narrow band gap of CdS, the toxicity and waste-management issues related to cadmium-containing auxiliary layers and the need for improved band alignment have motivated extensive research on CdS-free window and buffer layers. This review summarizes the main efforts devoted to replacing CdS in thin-film solar cells based on absorbers such as CdTe/CdSeTe, CIS, CIGS, CZTS, CZTSe, CZTSSe, Sb₂S₃, Sb₂Se₃, Sb₂(S,Se)₃, SnS and FeS₂. The most investigated alternative materials, including Zn(O,S), ZnS, In₂S₃, ZnMgO, ZnSnO, TiO₂, SnO₂ and SnS₂, are discussed with emphasis on their optical properties, band alignment, interface quality, deposition methods and impact on device performance. The analysis highlights that CdS replacement cannot be treated as a universal material substitution problem. Instead, each absorber and device architecture requires a specific front-interface design, where chemical compatibility, conduction band offset, defect passivation, optical transparency and process-induced interfacial modifications play a decisive role. CdS-free approaches are relatively mature for CdTe/CdSeTe- and CIGS-based solar cells, whereas kesterite absorbers, antimony chalcogenides and SnS still require further interface engineering. In FeS₂, by contrast, buffer-layer substitution remains secondary to the control of intrinsic surface and bulk electronic defects. This review provides a concise comparison of the most relevant CdS-free front/window materials and identifies key challenges for the future design of sustainable thin-film solar cells.

Keywords: thin-film solar cells; CdTe; CdSeTe; CIGS; CZTSSe kesterite; Sb₂(S,Se)₃; FeS₂; SnS; CdS-free buffer layers; band alignment



Academic Editor: James M. Gardner

Received: 22 June 2026

Revised: 20 July 2026

Accepted: 22 July 2026

Published: 24 July 2026

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1. Introduction

1.1. Thin-Film Photovoltaics and the Role of CdS

Thin-film photovoltaics emerged from the need to drastically reduce the amount of absorber semiconductor material required compared with crystalline silicon technology. This approach exploits direct-bandgap absorber materials with absorption coefficients on the order of 10^4 – 10^5 cm^{−1}, enabling the absorption of most of the useful solar spectrum within only a few hundred nanometres to a few micrometres of material thickness [1,2]. Among the most mature thin-film photovoltaic technologies are copper indium gallium

diselenide (CIGS) and cadmium telluride (CdTe). Emerging alternatives, motivated by the abundance of their constituent elements and their lower environmental impact, include $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) kesterites, antimony chalcogenides, tin sulfide (SnS) and iron disulphide (FeS_2) in the pyrite phase. A common feature of these technologies is their heterojunction architecture, in which a p-type absorber is coupled with a wider-bandgap n-type front-interface layer, buffer layer or electron-selective contact, together with a transparent conductive oxide (TCO) in either substrate or superstrate device configurations. Throughout this review, the term window layer refers to the transparent wide-bandgap semiconductor mainly responsible for optical transmission and carrier transport, whereas buffer layer denotes the thin semiconductor located between the absorber and the window layer, whose primary functions are heterojunction formation, band alignment and interface passivation. The term electron transport layer (ETL) is used for electron-selective contacts, particularly in oxide-based architectures, while front-interface layer is adopted as a broader term encompassing any material or engineered interfacial region contributing to junction formation, carrier selectivity or interface passivation. For historical and performance-related reasons, CdS has long been the benchmark n-type front/buffer layer in many of these devices, with typical thicknesses in the range of 40–80 nm [3]. CdS can be deposited using several techniques. Chemical bath deposition (CBD) remains the most widely employed laboratory method and has enabled record device efficiencies; however, CdS can also be deposited by thermal evaporation and, in particular, by sputtering [4]. Sputtering is a dry process that can be readily integrated into in-line manufacturing, scaled to industrial production and implemented without generating the cadmium-containing chemical wastes associated with CBD, which require costly treatment and disposal systems. Similarly, other CdS-free strategies based on vacuum deposition (e.g., sputtering or ALD) generally offer improved compatibility with industrial manufacturing and avoid liquid chemical waste, although their successful implementation requires careful control of thermal budget and low-damage deposition to preserve interface quality.

Consequently, the choice of deposition technique affects not only device performance but also process sustainability, an increasingly important aspect in the transition from laboratory-scale research to large-scale manufacturing.

1.2. Limitations of CdS

Despite its technological success, CdS has several limitations, including the toxicity of cadmium, parasitic absorption due to its relatively narrow band gap, and the need for improved band alignment and interface engineering in various absorber systems. Together, these limitations have stimulated extensive research on CdS-free front layer and buffer materials and, in selected absorber systems, on alternative junction architectures aimed at reducing or even eliminating the need for a CdS layer. It should also be emphasized that the meaning of CdS replacement is absorber-dependent. In CdTe/CdSeTe-based solar cells, for example, replacing CdS refers to the development of CdS-free front interfaces rather than to the elimination of cadmium from the device, since the absorber itself contains cadmium.

1.3. Challenges of CdS Replacement: Beyond Material Substitution

More broadly, moving beyond CdS does not necessarily mean simply replacing the CdS layer with another n-type window layer. In some absorber systems, a more radical strategy is to redesign the junction architecture itself by forming buried junctions or true homojunctions within the absorber through controlled doping or surface modification. This concept has been explored in CIGS, where surface doping with Zn enabled local conductivity-type conversion and buffer-free solar cells with efficiencies around 11.5% [5]. A related buried junction has also been observed in conventional CIGS/CdS devices, with

the electrically active junction located approximately 30–80 nm from the physical interface [6]. Similar buried-junction behaviour has also been reported in CdSeTe/CdTe solar cells, where interdiffusion and compositional grading contribute to an electrically active junction displaced from the nominal absorber/buffer interface [7]. Buried or quasi-buried homojunction phenomena have also been reported in CdS/Sb₂Se₃ and modified Sb₂Se₃ devices [8–10]. More recently, p-SnS/n-SnS homojunction solar cells have been demonstrated thanks to the development of n-type SnS, showing that CdS may become unnecessary when the junction can be formed directly within the absorber [11–13]. An additional aspect that deserves consideration is that CdS deposited by chemical bath deposition is not merely a passive buffer layer. In several absorber systems, particularly CIGS, CBD may induce Cd interdiffusion, near-surface doping and buried-junction formation, effects that contribute to interface passivation and favourable junction properties but are generally much less pronounced in dry-deposited alternative buffer layers. Consequently, successful CdS replacement often requires reproducing not only the electronic properties of CdS but also, where necessary, compensating for the beneficial chemical modifications introduced during interface formation. These examples broaden the concept of CdS replacement from a simple material-substitution problem to a more general strategy of interface and junction engineering.

1.4. Scope of This Review: Interface and Junction Engineering

This work adopts a critical review approach. For each absorber family, the discussion begins with the role of CdS and then examines the state of the art of Cd-free n-type buffer layers and, where experimentally demonstrated, alternative junction architectures such as buried junctions or homojunctions. Emphasis is placed on the underlying physical mechanisms, processing challenges and experimental results reported by different research groups. The motivation for moving beyond CdS is twofold. On the one hand, the RoHS Directive and REACH regulations encourage the elimination of cadmium from commercial devices. On the other hand, CdS (Eg ~2.42 eV) introduces parasitic absorption in the blue region of the solar spectrum (<520 nm), thereby limiting the short-circuit current density (Jsc), as illustrated in Figure 1a. Replacing CdS or, in selected architectures, eliminating it altogether, is therefore not only a way to reduce cadmium-containing auxiliary layers and related waste streams but also a route to improved device performance, provided that favourable band alignment, reduced parasitic absorption and effective interface passivation can be achieved at the junction [14]. As schematically illustrated in Figure 1b, the conduction-band offset (CBO) at the absorber/buffer interface is a key parameter governing charge separation and interface recombination. In general, a small positive CBO (spike) provides an energy barrier that suppresses interface recombination without significantly hindering electron transport, whereas a cliff-like alignment enhances interface recombination and typically reduces the open-circuit voltage. Therefore, the optimum CBO remains absorber- and device-dependent [15].

From a manufacturing perspective, replacing CdS should be evaluated not only in terms of environmental sustainability but also with respect to industrial transferability. Vacuum-based approaches such as sputtering and ALD eliminate the liquid chemical waste associated with CBD and are readily compatible with in-line manufacturing. Therefore, the central question addressed in this review is not simply which material can replace CdS, but rather how absorber-specific front-interface and junction engineering can reproduce or surpass the multiple electronic, optical and chemical functions historically provided by CdS.

The literature discussed in this review was selected from peer-reviewed publications indexed in major scientific databases (primarily Scopus, Web of Science, and Google

Scholar), with particular emphasis on studies published over the last 10–15 years while retaining seminal contributions that established the foundations of CdS-based heterojunctions and interface engineering. Representative device results reported in the comparative tables were selected based on their scientific relevance and the completeness of the reported photovoltaic parameters (V_{oc} , J_{sc} , FF and PCE). Preference was given to studies that illustrate representative front-interface engineering strategies or significant advances in device performance. Rather than providing a systematic review, the objective is to present a critical and representative overview of the evolution of CdS replacement strategies across the main p-type thin-film photovoltaic technologies.

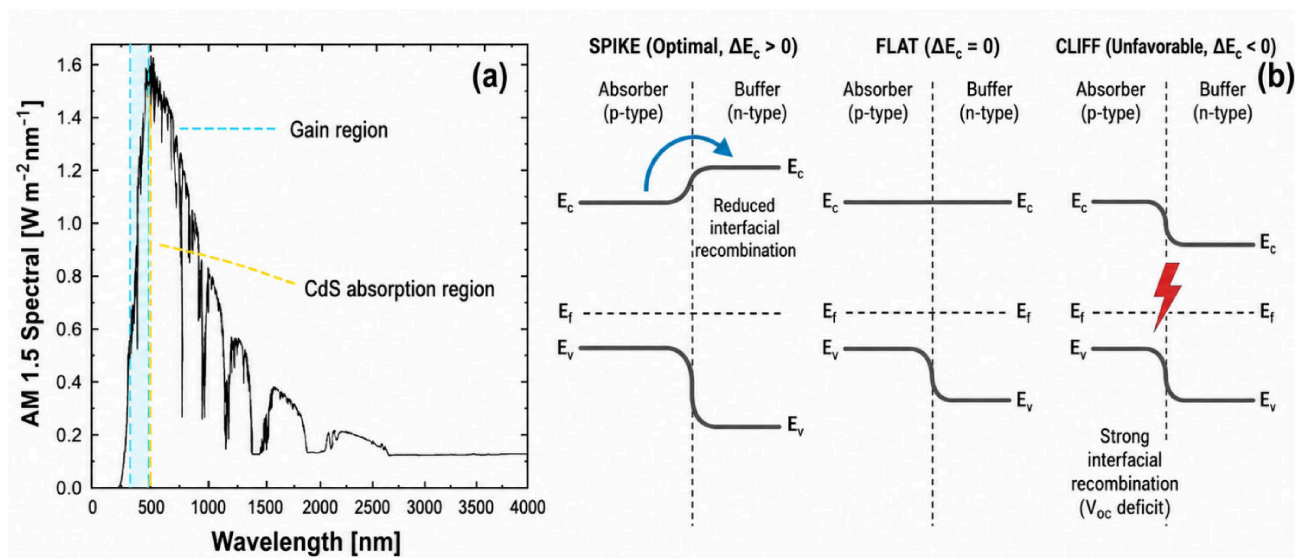


Figure 1. (a) Solar AM 1.5G spectral irradiance [16] highlighting the parasitic absorption region of a standard CdS buffer layer ($\lambda < 520$ nm) and the potential current gain region accessible by wider-bandgap CdS-free alternatives. (b) Schematic conduction band alignment configurations (CBO) at the absorber/buffer heterointerface: small positive spike ($\Delta E_c > 0$), ideal flat ($\Delta E_c = 0$), and unfavorable cliff ($\Delta E_c < 0$) promoting interface recombination. The band diagrams are schematic illustrations prepared by the authors and are not drawn to scale.

Within this framework, the effectiveness of CdS replacement ultimately depends on the dominant loss mechanisms of each absorber system. This absorber-specific perspective provides the conceptual basis for the comparative analysis developed throughout this review.

The main objectives are to reduce parasitic optical absorption and further optimize the front interface. In CIGS, kesterites, antimony chalcogenides and SnS, Cd-free alternatives are also pursued to improve environmental sustainability while tailoring band alignment, interface passivation and charge selectivity. By contrast, in absorber systems dominated by intrinsic material limitations, such as FeS₂, buffer layer engineering plays a secondary role compared with the control of bulk and surface defects. Accordingly, this review presents CdS replacement as an absorber-specific interface and junction engineering challenge rather than a simple material substitution, providing a unified framework for comparing mature and emerging thin-film photovoltaic technologies.

2. CdTe/CdSeTe Solar Cells: From CdS Buffer Layers to CdS-Free Front Interfaces

2.1. Historical Evolution and Role of CdS

CdTe is one of the most mature and commercially successful thin-film photovoltaic technologies, thanks to its near-optimal direct band gap of approximately 1.45 eV, high

optical absorption coefficient, and compatibility with large-area deposition processes. Conventional CdTe device architecture is based on a superstrate configuration, typically glass/TCO/n-type buffer/p-type CdTe/back contact. Historically, CdS has been used as the reference n-type buffer layer because it forms a robust heterojunction with CdTe, promotes favorable electronic selectivity, and is compatible with CdCl₂ activation treatment, essential for grain growth, defect passivation, and junction enhancement. However, CdS also introduces parasitic absorption at short wavelengths and can limit the achievable short-circuit current density when used at the thicknesses required for complete coverage and stable junction formation. The evolution of CdTe technology efficiency has been driven by several interconnected advances, including CdCl₂ activation, improved back contact engineering, doping with Cu or Group V elements, scaling of the CdSeTe/CdTe bandgap, and the replacement of CdS with wider bandgap front interface layers. The introduction of CdSeTe absorbers and advanced front buffers such as MgZnO or ZnO has enabled high current densities while preserving strong carrier selectivity at the front junction. More recently, As-doped CdSeTe/CdTe devices achieved a world-record efficiency of 22.3%, demonstrating that modern CdTe technology is now limited less by the CdS/CdTe junction itself and more by the combined optimization of absorber doping, lifetime, front interface recombination, and back contact stability [17].

2.2. CdS-Free Front Buffers and Interface Engineering

In CdTe-based solar cells, CdS substitution has a different meaning than in CIGS, kesterite, Sb₂(S,Se)₃, or SnS devices. Because the absorber itself contains cadmium, the transition to CdS-free front interfaces is driven primarily by optical and electronic considerations rather than the complete elimination of cadmium. The primary objectives are to reduce parasitic absorption in the blue spectral region, improve conduction band alignment at the front junction, suppress recombination at the interface, and maintain chemical compatibility with CdCl₂-activated CdTe or CdSeTe absorbers. Among the most studied CdS-free front interface materials, Mg_xZn_{1-x}O has played a central role. Its band gap, electron concentration, and conduction band position can be tuned by varying the Mg content, allowing for the design of the frontal interface barrier and recombination rate. However, MgZnO-based devices can exhibit anomalous J-V behavior, including S-kinks, when band alignment or contact selectivity are not properly optimized. Therefore, MgZnO is not simply a more transparent substitute for CdS, but an interface engineering layer whose composition and electronic properties must be tailored to the CdSeTe/CdTe absorber stack [18,19]. Highly resistive zinc oxide (ZnO) has also emerged as an effective CdS-free buffer for high-efficiency CdSeTe/CdTe devices. Recent ZnO/CdSeTe/CdTe solar cells have achieved efficiencies exceeding 21%, demonstrating that a wide bandgap oxide buffer can provide excellent optical transparency, stable device behavior, and a high-quality front interface when its thickness and coverage are properly controlled [20]. Recent group-V-doped Cd(Se,Te)/CdTe research cells have achieved a certified PCE of 23.1%, highlighting the continued progress of CdTe-based thin-film photovoltaics [21,22]. Other oxide-based strategies, including SnO₂ and Mg-doped SnO₂, have also been explored to reduce interface trap density, increase built-in potential, and improve front contact selectivity [23]. Overall, CdTe represents a relatively mature example where CdS can be widely substituted at the front interface, but successful CdS-free operation requires careful co-optimization of the transparent conductive oxide, buffer composition, absorber alloy, dopant activation, and post-deposition treatments. The main CdS replacement strategies reported for CdTe-based solar cells and their representative device performances are summarized in Table 1.

Table 1. Representative photovoltaic parameters of CdTe/CdSeTe solar cells employing Cd-containing benchmark buffer layers, CdS-derived front-interface strategies and fully CdS-free oxide front layers. The deposition method of the front layer is indicated in parentheses (CBD = chemical bath deposition; Sput. = magnetron sputtering; ALD = atomic layer deposition). The reported energy gap (Eg) refers to the absorber material. Certified efficiencies are marked with an asterisk (*). The values should be compared with caution because absorber composition, doping, front-stack design, activation treatment and back-contact engineering differ among the cited studies.

Absorber/Front Layer	Configuration/Main Role	Type	Eg (eV)	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)	Ref.
CdTe/CdS (CBD)	Conventional CdS benchmark heterojunction; long-established reference architecture for CdTe solar cells.	CdS benchmark	1.48	845	25.88	75.51	16.5	[24]
CdTe/CdS:O (CBD)	CdS benchmark window; CdS:O increases blue response, but CdS-related parasitic absorption below ≈ 520 nm remains a limitation.	Cd-containing benchmark	1.48	845	25.9	75.5	16.7	[25]
CdTe/Cd(Se,Te)/Mg _x Zn _{1-x} O (Sput.)	Composition-tunable CdS-free oxide buffer; front-interface barrier and MZO/Cd(Se)Te band alignment must be controlled to avoid abnormal J–V behaviour.	Fully CdS-free	≈ 1.4	854	28.4	79.1	19.1	[26]
CdTe/Cd(Se,Te)/SnO ₂ + Cd(O,S,Se,Te) (sput.)	SnO ₂ buffer with CdS-derived/intermixed pentenary front region; introduces a mild front bandgap gradient and reduces front-interface recombination.	CdS-derived interface strategy	≈ 1.4 –1.5	863	29.2	79.5	20.03	[27]
CdTe/Cd(Se,Te)/ZnO (sput.)	Highly resistive intrinsic ZnO buffer; wide-bandgap transparent CdS-free layer providing excellent Jsc and a high-quality front interface.	Fully CdS-free	1.41	875.5	30.43	80.48	21.44	[20]
CdTe/Cd(Se,Te)/SnO ₂ (Sput.)	CdS-free sputtered SnO ₂ buffer layer; improves front-interface passivation and electron selectivity, while optimized buffer thickness enhances junction quality and device performance.	Fully CdS-free	1.4	833	30.16	78.74	19.79	[28]
CdTe/Cd(Se,Te)/SnO ₂ /ZnO (sput.)	CdS-free oxide bilayer; improved front-interface passivation and electron selectivity relative to single oxide buffers.	Fully CdS-free	≈ 1.4 –1.5	882	30.3	81.0	21.7	[29]
CdTe or CdTe/Cd(Se,Te)/Mg-doped SnO ₂ (ALD)	CdS-free ETL concept; Mg doping of SnO ₂ increases built-in potential and reduces interfacial trap density, suggesting improved Voc and PCE.	Fully CdS-free	≈ 1.45	792	29.8	66.6	15.7	[23]
CdTe/As-doped Cd(Se,Te)/SnO ₂ :F	World-record CdS-free front interface; As-doped absorber and HR-ZnO maximize carrier collection and minimize front optical losses.	Fully CdS-free	≈ 1.4	888	31.9	78.6	22.3 *	[17]

3. CIGS: From CIS to Cadmium-Free Buffer Layers

3.1. Historical Evolution: From CuInSe₂ to Cu(In,Ga)(Se,S)₂

The progenitor of this absorber family is copper indium diselenide (CuInSe₂, CIS), a chalcopyrite semiconductor first synthesized in the 1950s. The first photovoltaic device based on this material was developed at Bell Laboratories using CIS single crystal coupled with a CdS window layer, achieving power conversion efficiencies (PCE) on the order of 12% [30]. The subsequent transition to polycrystalline thin films occurred during the 1980s, when CIS/CdS devices fabricated by co-evaporation surpassed PCEs of 10% [31]. Among the key innovations that established CIGS as one of the most efficient thin-film photovoltaic technologies, two are particularly relevant in the context of this review. The first is alloying with gallium, Cu(In_{1-x}Ga_x)Se₂: partial substitution of indium with gallium increases the bandgap from approximately 1.04 eV (CIS) up to ~ 1.68 eV (CuGaSe₂), enabling optimization of the open-circuit voltage (Voc) and spectral matching for $x \sim 0.3$ (Eg ~ 1.15 eV), as well as enabling bandgap grading along the absorber depth, which enhances carrier collection [32].

The second innovation is the three-stage co-evaporation process developed at NREL, together with the discovery of the beneficial role of sodium originating from soda-lime glass (SLG) substrates, which improves electrical conductivity and film microstructure [33]. The progression of record efficiencies reflects these advances: 19.9% (NREL, 2008) [34], followed by the surpassing of the 20% threshold and subsequent values of 20.8% and 21.7% reported by ZSW [35–37], up to record devices based on sulphur-selenium alloyed $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$ absorbers and Cd-free buffer layers developed by Solar Frontier, culminating in a certified PCE of 23.35% [38]. It is noteworthy that several of the highest certified CIGS efficiencies, reported in recent years, have been achieved using cadmium-free buffer layers, underscoring the maturity reached by these alternative materials.

3.2. The Dual Role of CdS: Heterojunction Formation, Doping Effects and Buried Junction Formation

CdS can fulfill multiple functions in CIGS solar cells, although the relative importance depends on the deposition technique employed:

- Junction formation. CdS forms a heterojunction with p-type CIGS, often characterized by a moderate spike-like conduction-band offset (CBO). When sufficiently small, this alignment promotes electron selectivity and helps suppress interfacial recombination without significantly hindering electron transport [39].
- Doping and buried junction formation (Figure 2). During chemical bath deposition, Cd^{2+} ions can interact with the Cu-poor near-surface region of CIGS, where copper vacancies are abundant. Cd incorporation into Cu-related sites may locally modify the defect chemistry and promote a partial conductivity-type conversion in the absorber surface region. This chemical modification is mainly confined to the outermost region of the CIGS surface, whereas the electrically active junction does not necessarily coincide with the physical CdS/CIGS interface. Cross-sectional potential measurements have shown that the main p–n junction can be located inside the CIGS absorber, several tens of nanometres away from the heterointerface, leading to the formation of a buried junction [6,40,41]. This interfacial modification is particularly favored during chemical bath deposition, where Cd^{2+} ions are readily available in solution and can partially react with the absorber surface.

This aspect is particularly relevant when evaluating Cd-free alternatives. Replacing CBD-grown CdS with a dry-deposited buffer layer does not simply modify the conduction-band alignment but may also eliminate the beneficial effects associated with Cd interdiffusion, near-surface doping and buried-junction formation. Consequently, successful Cd-free strategies should either reproduce these functions through alternative interface-engineering approaches or compensate for their absence by optimizing band alignment and interface passivation. In contrast, CdS deposited by thermal evaporation or sputtering tends to form a more abrupt physical heterojunction, with a less pronounced surface-doping effect. This distinction should be considered when comparing deposition routes, as dry processes, although more scalable and environmentally benign, may require additional interface engineering to recover the benefits associated with buried homojunction formation. By shifting the region of maximum recombination away from the defective interface, this mechanism contributes to the remarkable tolerance of CIGS devices to interfacial defects. Understanding this role of CdS is crucial when pursuing cadmium-free alternatives, since an effective replacement must either reproduce this doping-induced benefit or compensate for its absence through an appropriately engineered band alignment.

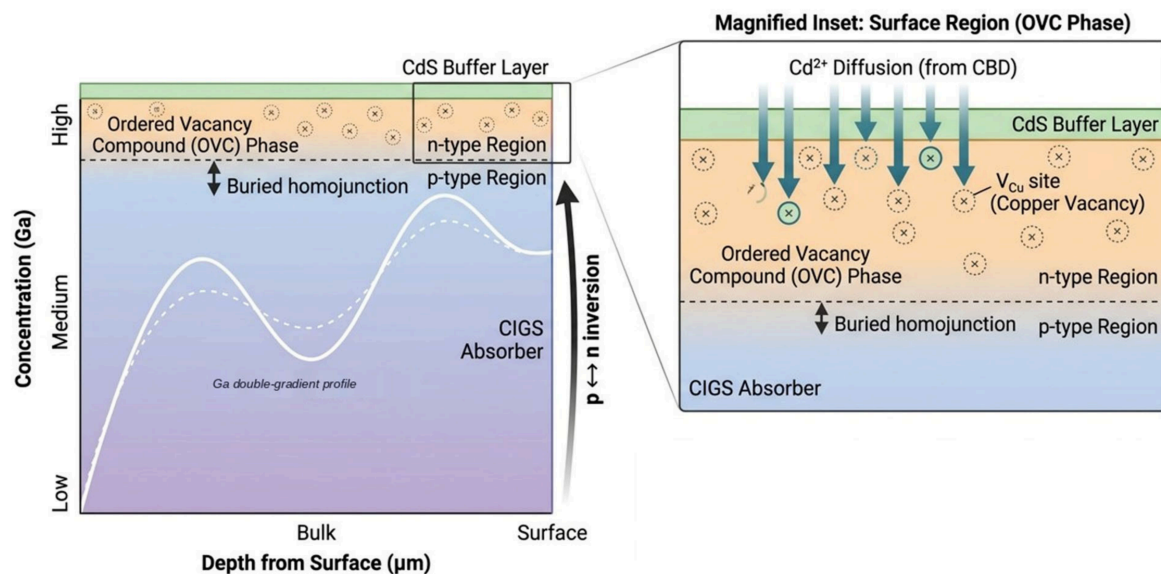


Figure 2. Not-to-scale schematic representation of the CIGS/CdS heterointerface showing the typical chalcopyrite depth-dependent bandgap grading (Ga double-gradient profile), the CBD-driven Cd diffusion/interdiffusion into the Cu-poor near-surface region of CIGS, and the resulting formation of a locally n-type region that can shift the electrically active p–n junction away from the physical CdS/CIGS interface, giving rise to a buried junction. This figure is an original schematic drawing prepared by the authors.

3.3. Cadmium-Free n-Type Buffer Layers for CIGS Solar Cells

Several CdS-free buffer layers have been investigated for CIGS solar cells, including Zn(O,S)-based compounds, Zn(O,S,OH), (Zn,Mg)O, In₂S₃, (Zn,Sn)O and related oxide or sulfide materials [14]. Their use is mainly motivated by the possibility of reducing parasitic absorption in the blue spectral region, tuning the conduction-band offset at the absorber/buffer interface and avoiding cadmium-containing wet-chemical processes. For Zn(O,S)-based layers in particular, the bandgap and conduction-band position can be adjusted by varying the O/S ratio, reducing optical losses and often increasing the short-circuit current density (J_{sc}) compared with CdS [42,43]. In₂S₃, instead, has been explored mainly as a cadmium-free sulfide buffer layer with relatively high optical transparency and compatibility with vacuum-based or low-temperature deposition processes, although its performance strongly depends on stoichiometry, defect chemistry and the resulting band alignment with CIGS [14,44]. The central challenge is the engineering of band alignment at the absorber/buffer interface. By varying the composition of Zn(O,S), the conduction-band offset (CBO) relative to CIGS can be tuned from a cliff configuration (negative offset), which is detrimental because it lowers the recombination barrier and consequently reduces V_{oc} , to a spike configuration (moderately positive offset), which is generally considered optimal. Excessively large positive offsets, however, can hinder carrier transport. The optimal processing window is therefore narrow and strongly dependent on the gallium content at the absorber surface [45]. A further challenge is metastable behavior. Many devices employing Cd-free buffer layers require light soaking to achieve their maximum efficiency and exhibit transient effects as well as cross-over phenomena in J–V characteristics. These effects are commonly attributed to charge states located at the absorber/buffer interface and within the buffer layer itself [46]. From a processing perspective, atomic layer deposition (ALD)-grown buffers, such as Zn(O,S) and (Zn,Mg)O, provide excellent conformality and low-temperature processing capability. Chemical bath deposition (CBD), however, remains highly competitive because of its low cost and scalability, while sputtered (Zn,Mg)O is particularly attractive for fully dry, in-line manufacturing integration. Experimental

results confirm the maturity of these approaches. Recent certified Cd-free CIGS record devices, reaching 23.35%, employ Zn(O,S,OH)-based buffer layers deposited by CBD, demonstrating that the elimination of cadmium does not entail a performance penalty and can, in fact, contribute to current-density gains through reduced optical losses [38]. Table 2 summarizes representative photovoltaic parameters reported in the literature. The optimal processing window is therefore narrow and strongly dependent on the gallium content at the absorber surface [45].

Table 2. Representative photovoltaic parameters reported for CIGS solar cells employing benchmark CdS and selected CdS-free buffer layers. The deposition method of the buffer layer is indicated in parentheses (CBD = chemical bath deposition; ALD = atomic layer deposition; Evap. = in-line evaporation). Certified efficiencies are marked with an asterisk (*). The reported energy gap (E_g) refers to the buffer layer material. The values are intended to highlight representative high-performance devices and should be compared with caution, since device architecture, absorber quality, deposition conditions and interface engineering differ among the cited studies.

Buffer Layer	Comment	E_g (eV)	$V_{(OC)}$ (mV)	$J_{(SC)}$ (mA/cm ²)	FF (%)	PCE (%)	Ref.
CdS (CBD)	Benchmark buffer layer for CIGS; strong junction quality and interface passivation, but parasitic blue absorption and cadmium use remain drawbacks.	2.4	741	37.8	80.6	22.6	[36]
Zn(O,S,OH)/Zn _{0.8} Mg _{0.2} O (CBD + ALD)	Certified world-record Cd-free CIGS buffer; wider bandgap reduces optical losses and can increase J_{sc} when CBO is properly optimized.	3.6	734	39.6	80.4	23.35*	[38]
(Zn,Mg)O (ALD)	Tunable oxide buffer for CBO control; performance is sensitive to Mg content, interface quality and transport barriers.	3.1–3.96	633	34	75	16.1	[47]
In ₂ S ₃ (Evap.)	Cd-free sulfide buffer compatible with dry or low-temperature processing; performance depends strongly on stoichiometry and CIGS band alignment.	2.0–3.6	673	36.3	74.5	18.2	[44]
(Zn,Sn)O (ALD)	Multicomponent oxide buffer with good transparency and compositional tunability; useful for ALD-based interface engineering.	3.5	666	31.73	69.3	14.7	[48]

4. CZTS/CZTSSe Kesterite Absorbers: Toward Earth-Abundant Thin-Film Photovoltaics

4.1. Beyond Standard CdS: Motivations and Limitations

$Cu_2ZnSn(S,Se)_4$ (CZTS and CZTSSe) kesterites were conceptually derived from CIGS by replacing the costly and less abundant elements indium and gallium with zinc and tin, while preserving a closely related crystal structure and a tunable direct bandgap, ranging from approximately 1.0 eV for the pure selenide to about 1.5 eV for the pure sulfide [49]. The photovoltaic properties of CZTS were first reported by Ito and Nakazawa in 1988, who demonstrated a heterodiode based on a transparent cadmium–tin oxide/CZTS structure. Thin-film CZTS solar cells were subsequently developed by Katagiri and co-workers using a Mo/CZTS/CdS/ZnO device architecture, with initial efficiencies below 1% [50,51]. A major breakthrough toward practically relevant performance was achieved through liquid-based processing. Todorov, Reuter and Mitzi reported a high-performance liquid-processed CZTSSe solar cell with an efficiency above 9.6% [52]. This was followed by the widely cited 12.6% CZTSSe device developed at IBM through a hydrazine-based solution-processing route [53], which remained a long-standing benchmark for kesterite photovoltaics for

about a decade. More recently, renewed progress in defect control, cation ordering and phase-evolution engineering has pushed CZTSSe efficiencies beyond this plateau, with a certified efficiency of 14.9% obtained through vacancy-enhanced cation ordering via Mg doping and a certified efficiency exceeding 15% achieved using a Li_2SnS_3 interphase strategy during selenization [54,55]. As in CIGS technology, CdS deposited by chemical bath deposition (CBD) is the benchmark buffer layer in kesterite solar cells, within a device architecture that is largely analogous to that of CIGS (substrate/Mo/absorber/CdS/i-ZnO/TCO). The fundamental limitation of kesterite devices does not primarily arise from the buffer layer itself, but rather from the large open-circuit voltage (V_{oc}) deficit relative to the Shockley–Queisser limit. This deficit is not governed by a single loss mechanism, but results from the combined contribution of bulk defect disorder, band tailing, secondary phases, rear-interface recombination and absorber/buffer interface losses. It is generally associated with Cu/Zn antisite disorder (CuZn and ZnCu antisite defects), which induces electrostatic potential fluctuations and band tailing; the multivalence of tin ($\text{Sn}^{2+}/\text{Sn}^{4+}$) and the formation of deep defects, particularly SnZn -related defects; secondary phases such as ZnS , Cu_2SnS_3 , and SnS(e) -based compounds; and rear-interface instabilities. At the rear interface, the formation of Mo(S,Se)_2 can be beneficial when thin and well controlled, but excessive or uncontrolled growth increases series resistance and may enhance rear-interface recombination [56,57]. Within this broader loss landscape, the CdS/CZTSSe interface remains important, but should be considered as one contribution among several. Nonideal band alignment, often tending toward a cliff-like conduction-band offset, as well as interfacial chemical reactions and defect formation at the absorber/buffer interface, can further enhance recombination losses. (Figure 3).

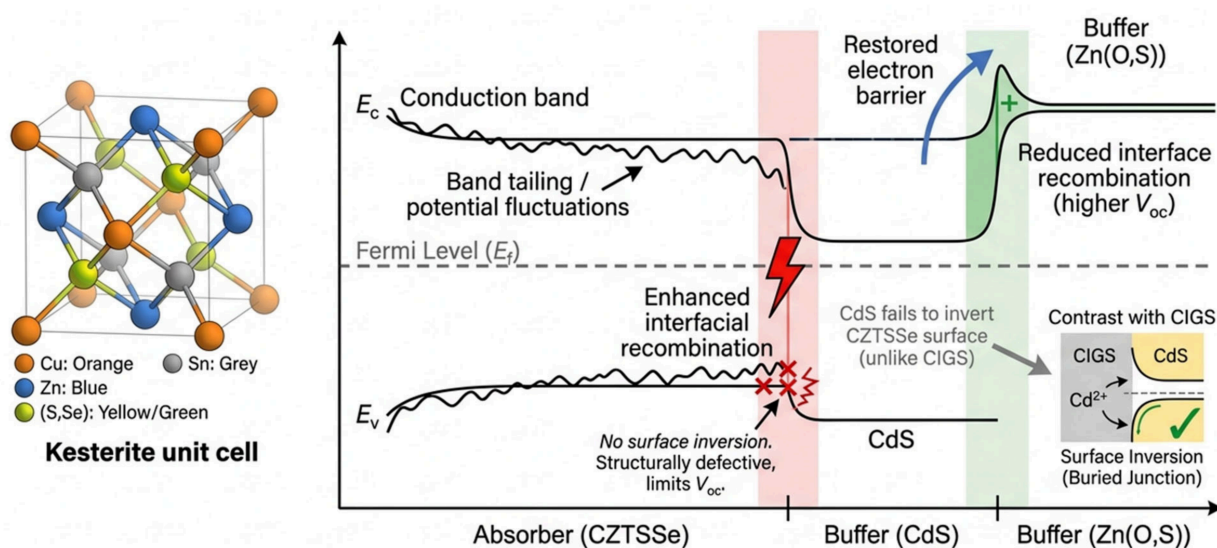


Figure 3. Energy diagram of a CZTSSe/CdS heterojunction illustrating the effect of Cu/Zn cation disorder on electrostatic potential fluctuations and electrostatic band tailing. The diagram contrasts the conventional CdS buffer layer, which fails to invert the kesterite surface and establishes an unfavorable cliff-like conduction band offset (CBO) that promotes severe interface recombination, with an alternative Zn(O,S) buffer configuration that successfully restores the electron transport barrier and mitigates the open-circuit voltage (V_{oc}) deficit. The inset explicitly highlights the comparative junction physics between CIGS and kesterites, illustrating how Cd^{2+} chemical bath interdiffusion drives a robust surface inversion (buried junction) exclusively in the CIGS system. The band diagrams are schematic illustrations prepared by the authors and are not drawn to scale.

Therefore, in kesterite solar cells, moving beyond CdS requires more than replacing a cadmium-containing buffer layer. Alternative buffers must simultaneously address optical

transparency, conduction-band alignment, interface passivation and chemical compatibility with an absorber that is intrinsically sensitive to defect disorder and secondary-phase formation.

4.2. Cadmium-Free Buffer Layers and Interface Engineering

Accordingly, numerous Cd-free buffer layers have been proposed for kesterite solar cells, each offering distinct advantages and limitations depending on their influence on band alignment, interface recombination and device fabrication. The most widely investigated fully Cd-free buffer layers include Zn(O,S), In_2S_3 and zinc–tin oxide compounds such as ZnSnO, whereas $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ represents an intermediate Cd-reduced strategy rather than a truly cadmium-free alternative [58]. Among these materials, Zn(O,S) is particularly attractive because its conduction-band position can be tuned by varying the O/S ratio, allowing the absorber/buffer CBO to be shifted, depending on the CZTSSe composition, from cliff-like toward a small positive spike-like configuration. However, the high defect density of kesterite absorbers often masks the benefits of improved interface energetics, and Cd-free buffer layers on CZTSSe devices frequently exhibit greater sensitivity to post-deposition thermal treatments [59–61]. The most significant advances have resulted from the combined engineering of both the absorber and the heterointerface. Yan et al. achieved efficiencies exceeding 10% in pure-sulfide CZTS devices through a heterojunction heat-treatment process that modifies the interfacial region [62]. Subsequent improvements in absorber and process engineering, particularly through optimization and control of selenium partial pressure during growth, have enabled CZTSSe devices to surpass 13% certified efficiencies [63]. More recently, certified efficiencies of 14.9% and above 15% have been demonstrated, showing that further progress in kesterite photovoltaics is being driven primarily by absorber and process engineering, including defect control, cation ordering, grain-growth regulation and selenization control [54,55]. However, these best-performing devices still underline the importance of achieving a high-quality absorber/buffer interface. Therefore, Cd-free buffers should not be evaluated only in terms of optical transparency or cadmium elimination, but also according to their ability to preserve interface passivation, favorable band alignment and chemical stability. It should therefore be emphasized that CdS replacement can realistically mitigate only the front-interface contribution to the overall Voc deficit by improving conduction-band alignment, reducing interface recombination and increasing optical transmission. However, the dominant losses associated with bulk disorder, electrostatic band tailing, Sn-related deep defects, secondary phases and rear-interface recombination remain largely unaffected by the choice of buffer layer. Consequently, further efficiency improvements require simultaneous optimization of absorber quality and interface engineering. For these reasons, research on Cd-free buffer layers for kesterite solar cells remains highly active and far from complete. Table 3 summarizes representative results reported in the literature.

Table 3. Representative photovoltaic parameters of CZTS/CZTSSe solar cells employing CdS benchmark buffers, fully Cd-free buffer layers and Cd-reduced buffer strategies. The reported energy gap (Eg) refers to the absorber material. The values should be compared with caution because absorber composition, bandgap, device architecture and post-deposition treatments differ among the cited studies.

Absorber/BL	Comment	Eg (eV)	Voc (mV)	Jsc (mA/cm ²)	FF (%)	PCE (%)	Ref.
CZTSSe/CdS (CBD)	Historical CZTSSe benchmark; high efficiency mainly reflects hydrazine-based absorber quality rather than CdS replacement.	1.13	513	35.2	69.8	12.6	[53]
CZTS/CdS (CBD)	Pure-sulfide reference; heterojunction heat treatment modifies the interfacial region and improves voltage output.	1.5	730	21.74	69.27	11.01	[62]

Table 3. Cont.

Absorber/BL	Comment	E _g (eV)	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)	Ref.
CZTSSe/CdS (CBD)	High-efficiency CdS benchmark; performance is mainly driven by absorber/process engineering and selenium partial-pressure control.	1.1	551.2	35.7	71.7	14.13	[63]
CZTSSe/Zn(O,S) (CBD)	Fully Cd-free buffer; tunable CBO, but performance remains sensitive to interface recombination and post-deposition treatments.	1.1	496	35.6	56	9.82	[64]
CZTS/Zn _{1-x} Cd _x S (CBD)	Cd-reduced rather than fully Cd-free strategy; Cd incorporation helps tune band alignment and preserve high V _{oc} in CZTS.	1.5	747.8	19.5	63.2	9.2	[65]

5. Antimony Chalcogenide Absorbers: Ribbon Orientation and Cd-Free Interface Engineering

5.1. Crystal Anisotropy and Ribbon Orientation in Sb₂(S,Se)₃ Absorbers

Antimony chalcogenides are emerging absorber materials characterized by a strongly anisotropic quasi-one-dimensional crystal structure consisting of covalently bonded (Sb₄X₆)_n ribbons (X = S, Se) held together by weak van der Waals interactions. As depicted in Figure 4, this structural anisotropy has profound implications for charge transport: carriers move efficiently along the ribbon direction, whereas transport across adjacent ribbons is hindered by van der Waals gaps. Consequently, carrier collection, defect formation and interface recombination are strongly affected by the crystallographic orientation of the absorber, making ribbon orientation a key parameter governing photovoltaic performance [66,67]. It should also be noted that antimony chalcogenide solar cells can be fabricated in both substrate and superstrate configurations [66]. In superstrate devices, the Sb₂(S,Se)₃ absorber grows directly on the buffer or electron-transport layer; therefore, this underlying layer can influence not only band alignment and electron extraction, but also absorber nucleation, grain morphology and ribbon orientation [68–70]. In substrate devices, by contrast, the absorber is grown first on the back contact or seed layer, and the buffer layer is deposited afterwards. In this case, the buffer mainly affects the already-formed absorber surface through band alignment, interface passivation and chemical stability [71], whereas ribbon orientation is primarily governed by the back contact, seed layer and absorber growth conditions.

From an efficiency-evolution perspective, Sb₂Se₃ photovoltaics have progressed rapidly over the last decade: after early devices with efficiencies around 1–2%, the recognition of oriented quasi-one-dimensional ribbons and benign grain boundaries established the structural basis for higher-performing cells, followed by certified Sb₂Se₃ devices reaching 6.5% and 7.6% efficiency [72–74]. More recent advances in deposition kinetics, texture control, defect passivation and contact/interface engineering have pushed Sb₂Se₃ devices beyond the 10% threshold, with reported efficiencies of 10.12% and 10.57%, while Sb₂(S,Se)₃ solar cells have also recently reached certified efficiencies around 10.7% [75–77]. The bandgap can be tuned from approximately 1.1–1.3 eV for Sb₂Se₃ to about 1.7 eV for Sb₂S₃, while the alloy Sb₂(S,Se)₃ covers the intermediate range that is particularly attractive for single-junction solar cells [74]. Additional advantages of this material family include the relatively low toxicity and abundance of its constituent elements, the binary or ternary single-phase composition, which largely avoids the secondary-phase issues that plague kesterite absorbers, the high optical absorption coefficient, and good chemical stability. Historically, the first thermally evaporated thin-film Sb₂Se₃ solar cell employing a CdS/Sb₂Se₃ heterojunction achieved a power conversion efficiency of 1.9% [78]. Subsequent progress, including core-shell nanorod architectures with efficiencies around 9.2% [79] and planar or vapor-transport-deposited absorbers exceeding the 10% threshold [75], confirmed that

performance improvements are strongly linked to absorber morphology, ribbon orientation and interface control. Therefore, CdS remains the benchmark n-type layer for antimony chalcogenide solar cells, particularly in superstrate architectures where it can influence both junction formation and absorber growth. However, because device performance is strongly affected by ribbon orientation, surface termination and interfacial defect passivation, CdS replacement in antimony chalcogenide solar cells cannot be considered independently from absorber growth and interface control.

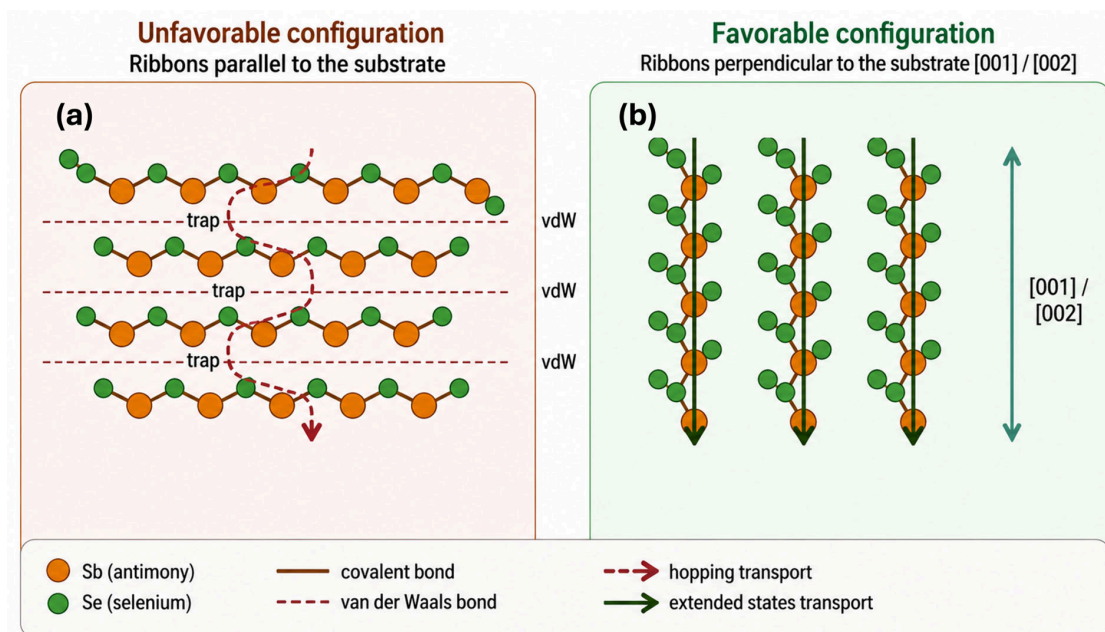


Figure 4. Schematic representation of the anisotropic crystal structure and transport pathways in quasi-one-dimensional Sb_2Se_3 thin-film solar cells. (a) Unfavourable horizontal growth, where covalent ribbons lie parallel to the substrate, forces charge carriers to cross van der Waals gaps and can promote hopping transport through defect-rich regions. (b) Favourable vertical growth along the [001] or [002] direction aligns the covalently bonded ribbons perpendicular to the substrate, favouring extended-state transport, efficient carrier extraction and reduced recombination losses. This figure is an original schematic drawing prepared by the authors.

5.2. Cadmium-Free Electron Transport Layers and Interface Engineering

Given the relatively early stage of $\text{Sb}_2(\text{S,Se})_3$ photovoltaic technology, the replacement of CdS has been explored in parallel with absorber optimization, particularly with respect to ribbon orientation, surface chemistry and interface passivation. The impact of Cd-free buffer and electron-transport layers on device performance differs significantly between superstrate and substrate architectures. In superstrate $\text{Sb}_2(\text{S,Se})_3$ solar cells, the ETL directly affects absorber nucleation and growth; therefore, Cd-free layers such as TiO_2 , SnO_2 or ZnO can influence not only electron extraction and band alignment, but also grain morphology, ribbon orientation and defect density. As a result, improvements in J_{sc} and FF are often linked to enhanced vertical carrier transport, reduced shunting paths and better electron selectivity. In substrate configurations, where the absorber is already formed before buffer deposition, Cd-free layers mainly affect V_{oc} and FF by modifying the front-interface recombination velocity, passivating surface defects and tuning the conduction-band offset. However, these layers must also avoid chemical damage or excessive interdiffusion during deposition or post-treatment, since an otherwise favourable band alignment can be offset by interface degradation. Thus, the same Cd-free material may lead to different performance trends depending on whether it acts as a growth-directing underlayer in superstrate devices or as a post-deposited passivating/selective contact in

substrate devices. Cd-free electron transport layers (ETLs) investigated for $\text{Sb}_2(\text{S,Se})_3$ -based solar cells include TiO_2 , SnO_2 , ZnO , and related wide-bandgap oxides, which are typically employed in superstrate configurations [80]. A comprehensive challenge in these systems is interface energetics: band alignment at the ETL/absorber junction is strongly dependent on the S/Se ratio, which simultaneously tunes both the bandgap and the absolute band-edge positions. In particular, a cliff-like CBO can enhance interfacial recombination and limit the V_{oc} , whereas a small positive (spike-like) offset is generally more favorable for efficient carrier extraction. Although TiO_2 and SnO_2 provide excellent optical transparency and chemical stability, their band alignment with $\text{Sb}_2(\text{S,Se})_3$ is not always optimal compared with CdS, making interfacial engineering essential for performance optimization. Strategies such as surface modification of CdS, interfacial passivation, and heterojunction tuning have therefore played a key role in device improvement [81]. Regarding device performance, $\text{Sb}_2(\text{S,Se})_3$ solar cells have reached a major milestone with a certified power conversion efficiency (PCE) of 10.0% under hydrothermal processing, as reported by Tang et al. [82]. This result established $\text{Sb}_2(\text{S,Se})_3$ as a competitive emerging thin-film photovoltaic absorber. Subsequent improvements in absorber quality, crystallographic orientation, and interfacial engineering have enabled further incremental gains in device performance beyond this threshold [81,82]. In particular, recent work has demonstrated that thermally induced structural ordering combined with MgCl_2 -assisted atomic-scale defect passivation can substantially suppress deep-level defects, extend carrier lifetime and improve the electronic quality of Sb_2Se_3 absorbers, further highlighting the importance of coupling absorber optimization with interface engineering [83]. Notably, the highest-performing devices reported to date still rely predominantly on CdS as the electron transport layer, highlighting that CdS remains the benchmark interfacial material. This emphasizes that the development of fully competitive Cd-free ETLs requires simultaneous optimization of band alignment and interfacial passivation to replicate the beneficial electronic properties currently provided by CdS. Table 4 summarizes representative results reported in the literature. More recently, the demonstration of an internal homojunction Sb_2Se_3 solar cell has further expanded the concept of CdS-free junction engineering. Rather than relying on a conventional heterojunction with an external electron-transport layer, this approach creates the p-n junction directly within the absorber through polarity control, simultaneously strengthening the built-in electric field and reducing non-radiative recombination. These results further support the idea that future Sb_2Se_3 photovoltaics may progressively evolve from simple buffer-layer replacement toward absorber-integrated junction engineering [10].

Table 4. Representative photovoltaic parameters of antimony chalcogenide (Sb_2Se_3 and $\text{Sb}_2(\text{S,Se})_3$) solar cells employing Cd-containing benchmark ETL/buffer layers and Cd-free ETL/buffer configurations. The deposition method of the front-interface layer is indicated in parentheses (Thermal evap. = thermal evaporation; CBD = chemical bath deposition; ALD = atomic layer deposition; Spin = spin coating). The reported energy gap (Eg) refers to the absorber material. The values should be compared with caution because absorber composition, deposition conditions, device architecture (planar or nanostructured), front-interface design and back-contact engineering differ among the cited studies.

Absorber/BL	Configuration/Main Role	Eg (eV)	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	Ref.
$\text{Sb}_2\text{Se}_3/\text{CdS}$ (Thermal evap.)	CdS benchmark; mainly superstrate heterojunction. Historical baseline for Sb_2Se_3 devices.	1.2	300	13.2	48	1.9	[78]
$\text{Sb}_2\text{Se}_3/\text{CdS-TiO}_2$ bilayer (CBD + ALD)	CdS benchmark; nanorod/structured architecture. Efficiency gain mainly reflects improved carrier collection.	1.2	400	32.58	70.3	9.2	[79]

Table 4. Cont.

Absorber/BL	Configuration/Main Role	Eg (eV)	Voc (mV)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)	Ref.
Sb ₂ (S,Se) ₃ /CdS (CBD)	CdS benchmark; mainly superstrate. Performance depends on absorber quality, S/Se ratio, ribbon orientation and interface recombination.	1.3–1.5	655	24.1	63.5	10.0	[82]
Sb ₂ (S,Se) ₃ /CdS (CBD)	CdS benchmark with interface engineering. Highlights the need to reproduce CdS-related band alignment and passivation benefits.	1.3–1.5	678	23.63	66.07	10.3	[81]
Sb ₂ Se ₃ /TiO ₂ (Spin)	Fully Cd-free ETL; mainly superstrate. Growth-directing underlayer and electron-selective contact; affects morphology, vertical ribbon orientation and shunt suppression.	1.2	368	27.4	49.1	4.95	[80]
Sb ₂ Se ₃ /SnO ₂ -TiO ₂ (Spin)	Fully Cd-free oxide ETL; mainly superstrate. Transparent and chemically stable contact; interfacial modification can improve extraction and reduce recombination.	1.2	335	25.3	47.2	4.0	[84]
Sb ₂ Se ₃ /ZnO (ALD)	Fully Cd-free buffer/ETL; mainly superstrate. Stable wide-bandgap contact; performance depends on compactness, band alignment and front-interface recombination.	1.2	391	26.2	57.8	5.93	[85]

6. Interface Engineering in SnS Solar Cells

In the case of SnS-based solar cells, the comparison between CdS, alternative buffers, and possible homojunctions clearly shows that the main issue is not only the replacement of a cadmium-containing material, but also the control of the interface and band alignment. SnS/CdS devices have long been the experimental benchmark, since CdS enables the formation of an n-CdS/p-SnS heterojunction capable of separating photogenerated charges and providing a reasonable electronic selectivity; in particular, SnS/CdS cells based on absorbers grown by vapor transport deposition have achieved a certified efficiency of 4.225%, attributed to the improvement of the heterointerface quality and the reduction in interfacial defects by optimizing TCO deposition or direct annealing of the SnS/CdS interface at 300 °C [86]. However, the same study still highlights significant Jsc losses due to recombination and a high defect density associated with Sn and S vacancies, exceeding 10¹⁷ cm⁻³, indicating that CdS is not sufficient to overcome the intrinsic and interfacial electronic limitations of SnS [86]. In this context, alternative buffers such as Zn(O,S), Zn_{1-x}Mg_xO, and more recently ZnSnO have been investigated not only to eliminate cadmium, but above all to modulate the conduction band offset, improve optical transparency, and reduce recombination at the interface. Sinsermsuksakul et al. showed that increasing the sulfur content in Zn(O,S) allows to drive the CBO towards slightly positive values, obtaining a SnS/Zn(O,S) cell with S/Zn = 0.37, Jsc = 19.4 mA cm⁻², Voc = 0.244 V, FF = 42.97% and NREL certified PCE of 2.04% [87], while Ikuno et al. experimentally controlled the CBO by varying the Mg content in Zn_{1-x}Mg_xO, identifying the optimal range of values between -0.1 and 0 eV and obtaining efficiencies of about 2.1% [88]. Further progress has been reported by Park et al., who achieved an efficiency of 2.9% by co-optimizing the SnS absorber and the Zn(O,S) buffer [89], while more recent results on ALD-deposited ZnSnO buffers confirm the interest in Cd-free layers capable of combining chemical control of the interface, transparency and electronic selectivity [90]. In parallel, an even more radical approach is represented by p-SnS/n-SnS homojunctions, which would eliminate the chemical discontinuity typical of heterojunctions; This strategy has historically been limited by the difficulty of obtaining stable n-type SnS, but the realization of a p-SnS/n-SnS homojunction by deposition of a polycrystalline p-type SnS film on Cl-doped n-type SnS single crystal

yielded $V_{oc} = 360$ mV, $J_{sc} = 7.5$ mA cm⁻², FF = 53% and a PCE of 1.4%, with a built-in potential of 0.92 eV near the SnS gap, suggesting a potential advantage in terms of open-circuit voltage [13]. Subsequent advances in n-type conduction of SnS, achieved in thin films by Cl doping and stoichiometry control via sulfur plasma, together with studies on Fermi-level pinning, band bending and SnS/MoO₃ interfaces, indicate that improved performance will require not only more transparent and sustainable buffers, but above all a careful control of surface states, interfacial recombination and band alignment [12,91]. Table 5 summarizes representative photovoltaic parameters reported for SnS solar cells employing conventional CdS heterojunctions, Cd-free buffer layers and homojunction architectures.

Table 5. Representative photovoltaic parameters of SnS solar cells employing the conventional CdS buffer layer, selected Cd-free buffer layers and homojunction architectures. The deposition method of the front-interface layer is indicated in parentheses (CBD = chemical bath deposition; ALD = atomic layer deposition; Sput. = magnetron sputtering). The values should be compared with caution because absorber quality, defect density, band alignment, interface passivation and junction architecture (heterojunction or homojunction) differ among the cited studies.

Absorber/Junction	Comment	Buffer/Strategy	Key Feature	V _{oc} (mV)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)	Ref.
SnS/CdS (CBD)	Highest certified SnS/CdS value cited here; improvement linked to heterointerface quality, but J _{sc} losses and high defect density remain limiting.	CdS	Benchmark heterojunction	346	20.76	58.76	4.22	[86]
SnS/Zn(O,S) (ALD)	Demonstrates band-offset engineering; S/Zn = 0.37 shifted the CBO toward slightly positive values.	Zn(O,S)	Cd-free CBO tuning by S/Zn ratio	244	19.4	42.97	2.04	[87]
SnS/Zn _{1-x} Mg _x O (Sput.)	Optimal CBO identified around -0.1 to 0 eV; useful for understanding the narrow band-alignment window in SnS devices.	Zn _{1-x} Mg _x O	Cd-free CBO tuning by Mg content	270	12.1	64	2.1	[88]
SnS/Zn(O,S) (ALD)	Shows that buffer replacement must be coupled with absorber optimization rather than treated as a standalone substitution.	Zn(O,S)	Co-optimized absorber/buffer	261	24.9	44.4	2.9	[89]
SnS/ZnSnO (ALD)	Recent interface-engineering strategy; combines transparency, conformality and compositional control.	ZnSnO	ALD Cd-free oxide buffer	430	19.62	48.3	4.07	[90]
p-SnS/n-SnS (homojunction)	Radical alternative to heterojunctions; removes chemical discontinuity, but performance is still limited by control of n-type SnS and interface/surface states.	Homojunction	CdS-free junction architecture	360	7.5	53	1.4	[13]

7. Pyrite (FeS₂): Promise and Intrinsic Limitations

Pyrite (cubic FeS₂) has long been considered one of the most theoretically promising absorber materials for thin-film photovoltaics. It combines a relatively favorable narrow bandgap of approximately 0.95 eV with an exceptionally high optical absorption coefficient (>10⁵ cm⁻¹ above the band edge), enabling efficient photon harvesting at sub-micrometer thicknesses. In addition, its constituent elements are among the most abundant and low-cost in the Earth's crust, making FeS₂ an appealing candidate for terawatt-scale photovoltaic deployment from a materials availability perspective [92,93]. Early studies, particularly in

the context of photoelectrochemical energy conversion, demonstrated strong light absorption and significant photocurrent generation, establishing the fundamental feasibility of pyrite-based solar energy conversion. Historically, FeS₂ attracted strong interest because early photoelectrochemical and Schottky-type devices confirmed efficient light absorption and photocurrent generation, but subsequent solid-state photovoltaic devices failed to translate these favourable optical properties into high open-circuit voltages or competitive efficiencies. This was followed by extensive experimental efforts in the 1990s and early 2000s aimed at realizing solid-state photovoltaic devices. Despite this long-standing research interest, pyrite has consistently failed to progress beyond very low device efficiencies [92,93]. The central limitation of FeS₂ lies in the severe mismatch between its excellent optical properties and its poor electronic quality. While photocarrier generation is highly efficient, device open-circuit voltages remain extremely low (typically on the order of a few hundred millivolts), corresponding to only a small fraction of the theoretical Shockley–Queisser limit [92]. This behavior reflects fundamental electronic losses that are intrinsic to the material rather than purely interfacial engineering issues. A key factor responsible for this performance collapse is the presence of a high density of intrinsic defect states, particularly sulfur vacancies and deep donor-like surface states. These defects induce strong Fermi-level pinning and lead to the formation of a surface inversion layer, which effectively short-circuits the photovoltaic junction and suppresses the achievable photovoltage [92,94]. Recent experimental evidence has also revealed the existence of an internal p–n junction within pyrite single crystals, providing a possible explanation for the anomalously low open-circuit voltages observed in FeS₂ solar cells [95]. In addition, FeS₂ exhibits a pronounced tendency to form secondary iron sulfide phases such as marcasite, pyrrhotite, and non-stoichiometric FeS_x during synthesis, further complicating phase control and electronic passivation [92,93]. Finally, significant deviations between bulk and surface stoichiometry contribute to non-uniform band bending and additional recombination pathways [92]. Within this framework, the role of n-type buffer layers and CdS replacement strategies assumes a fundamentally different significance compared with CIGS, kesterites, and antimony chalcogenides. In those systems, device performance is strongly governed by interfacial band alignment, conduction-band offset engineering (cliff vs. spike), and buffer-mediated passivation effects. In contrast, for FeS₂ the dominant bottleneck is not interface optimization but the inability of the absorber surface itself to sustain a well-defined and stable photovoltaic junction. As a result, discussions on CdS or Cd-free buffer layers are largely secondary at the current stage of development. Consequently, research efforts in pyrite photovoltaics are primarily directed toward defect engineering, surface chemistry control, and phase stabilization strategies rather than buffer layer substitution. This places FeS₂ in a fundamentally different regime compared with the other thin-film absorber families discussed in this review, highlighting that the effectiveness of Cd-free window layer strategies is ultimately constrained by the intrinsic electronic quality of the absorber material. Therefore, unlike the other absorber families discussed in this review, FeS₂ does not currently provide a meaningful platform for comparing CdS and Cd-free buffer layers in terms of device performance. Any future role of alternative n-type contacts will become relevant only if defect density, surface stoichiometry, Fermi-level pinning and phase purity can first be brought under sufficient control. Table 6 summarizes representative photovoltaic parameters reported for FeS₂ solar cells, highlighting that device performance remains primarily limited by intrinsic material properties rather than by the choice of the front-interface layer.

Table 6. Main performance-limiting mechanisms in FeS₂ pyrite photovoltaics and their implications for Cd-containing and Cd-free front-interface strategies. The table summarizes the dominant absorber-intrinsic, surface-electronic and materials-related limitations governing FeS₂ photovoltaic performance. Unlike the other absorber systems discussed in this review, device performance is presently controlled primarily by absorber quality, surface electronic structure and phase stability rather than by the choice of the front-interface layer. Therefore, direct comparisons between CdS and Cd-free front-interface layers should be interpreted with caution.

Limiting Factor	Comment	Physical Effect	Impact on Device Performance	Implication for CdS/Cd-Free Buffers	Ref.
Sulfur vacancies and deep donor-like defects	Primary intrinsic bottleneck; explains why FeS ₂ does not behave like a conventional interface-limited absorber.	High density of intrinsic surface and bulk defect states; donor-like surface states promote strong Fermi-level pinning.	Severely suppresses Voc and increases non-radiative recombination despite strong optical absorption.	Changing the n-type buffer alone is unlikely to recover high voltage unless defect density and surface states are first controlled.	[92,94]
Surface inversion layer	Surface chemistry and passivation are prerequisites before meaningful buffer comparison.	Pinned Fermi level can induce surface inversion and uncontrolled band bending at the absorber surface.	May effectively short-circuit the photovoltaic junction and limit the achievable photovoltage.	A CdS or Cd-free contact cannot define an efficient junction if the FeS ₂ surface already imposes an unfavorable electronic structure.	[92,94]
Secondary iron sulfide phases	Phase control is a materials-growth problem rather than a front-buffer problem.	Formation of marcasite, pyrrhotite and non-stoichiometric FeS _x during synthesis.	Reduces phase purity, reproducibility and electronic quality; introduces additional recombination pathways.	Cd-free buffer optimization is secondary until phase stability and stoichiometry are reproducibly controlled.	[92,93]
Surface/bulk stoichiometry mismatch	Highlights the need for surface reconstruction/passivation before contact engineering.	Deviation between bulk and surface composition produces non-uniform band bending and unstable surface energetics.	Adds recombination losses and prevents formation of a stable selective contact.	Alternative contacts may fail if deposited on a chemically unstable or non-stoichiometric FeS ₂ surface.	[92]
Internal p-n junction in FeS ₂ crystals	Further supports the view that FeS ₂ is not yet a mature platform for CdS vs. Cd-free buffer benchmarking.	Uncontrolled internal junction formation has been observed in pyrite single crystals.	Can contribute to anomalously low Voc and complicate interpretation of external heterojunction behavior.	The externally deposited buffer may not be the dominant junction-controlling element.	[95]
Overall absorber electronic quality	FeS ₂ should be discussed as a limiting case where absorber-intrinsic physics dominates over buffer substitution.	Excellent absorption is not matched by adequate carrier lifetime, surface stability and junction control.	Very low solid-state photovoltaic efficiencies persist despite attractive optical properties.	Future Cd-free contacts will become relevant only after defect passivation, surface chemistry control and phase stabilization improve absorber quality.	[92,93]

8. Discussion: The Unifying Role of Band Alignment and the Limits of CdS Replacement

To facilitate a consistent comparison among the different absorber families, the discussion is based on a comparative framework comprising four key aspects: (i) band alignment at the heterojunction, (ii) interface recombination and defect passivation, (iii) junction formation and charge-selective transport, and (iv) the resulting impact on photovoltaic performance. Although the relative importance of these factors varies among material systems, this framework provides a consistent basis for comparing mature and emerging thin-film photovoltaic technologies and for highlighting the absorber-specific challenges associated with moving beyond CdS. Analyzing the families of absorbers examined in this review (CdTe/Cd(Se,Te), CIGS, kesterites, antimony chalcogenides, SnS, and iron pyrite), a common physical principle emerges: thin-film photovoltaic performance is strongly influenced by the interplay between band alignment at the interface, selective charge transport, and defect passivation. However, the importance of these factors varies greatly from one material system to another. Across these diverse technologies, the establishment of a small, positive conduction-band offset (CBO), typically within a narrow window of approximately +0.1 to +0.3 eV (a moderate “spike”), represents the universal energetic optimum to ensure high selectivity while minimizing interface recombination. Such a moderate spike acts as an energy barrier for minority carriers, thereby suppressing their

recombination at the absorber/front-interface layer interface while remaining sufficiently low to allow efficient electron transport by thermionic emission. In contrast, a cliff-like CBO lowers the interfacial recombination barrier, increasing electron-hole recombination and consequently reducing the open-circuit voltage (Voc). Consequently, mature technologies such as CdTe/Cd(Se,Te) and CIGS already demonstrate that front-interface engineering can enable the partial or complete replacement of CdS without compromising device performance, whereas in emerging absorbers the effectiveness of CdS replacement remains closely linked to absorber quality, defect chemistry, junction formation and surface stability. CdTe/Cd(Se,Te) represents a special case because replacing CdS does not eliminate cadmium from the device, but replaces the CdS window/buffer layer with wider-bandgap electron-selective front-interface materials. In this architecture, precise tuning of the Mg content is key to shifting the interface from an unfavorable negative cliff (-0.10 eV for pure ZnO) to an optimized positive spike ($+0.20$ eV at $x \approx 0.15$), whereas excessive alloying ($x > 0.35$) triggers an insurmountable electron barrier up to $+0.32$ eV [96]. This example illustrates how the success of CdS-free CdTe architectures relies not only on replacing the buffer layer, but also on carefully engineering the front-interface band alignment to preserve the electronic functionality originally provided by CdS while reducing parasitic absorption. In CIGS technology, cadmium-free buffer layers have reached an even greater level of maturity. Materials such as Zn(O,S) and related oxides can achieve performance equal to that of CdS, and in some cases, slight improvements, primarily through reduced optical losses and optimized peak-shaped conduction band alignment. By carefully manipulating the S/(O + S) ratio, researchers can successfully transition away from the severe cliff alignments of unalloyed ZnO and position the CBO within the favorable $+0.1$ eV to $+0.3$ eV spike window [97]. In this system, interface engineering has advanced enough to effectively replace CdS in several cutting-edge architectures without compromising efficiency. A different situation exists in kesterite solar cells. Although Cd-free buffers, such as Zn(O,S), In_2S_3 , and $(\text{Zn,Sn})\text{O}$, can improve band alignment and reduce parasitic absorption, notably by replacing the unfavorable cliff alignment typical of conventional CdS/CZTS interfaces (frequently reported between -0.18 eV and -0.24 eV) with a tailored spike, provided that excessive sulfur accumulation is restricted to avoid massive transport barriers [98], the main limitation remains the high open-circuit voltage deficit associated with cationic disorder, defect formation, and electrostatic potential fluctuations. Consequently, buffer layer optimization alone is insufficient to close the efficiency gap with the Shockley-Queisser limit, and CdS-based references still dominate many high-performance devices. For antimony chalcogenides, including Sb_2Se_3 and $\text{Sb}_2(\text{S,Se})_3$, device performance is controlled by both interface energetics and anisotropic charge carrier transport. Their one-dimensional, ribbon-like crystalline structure makes crystallographic orientation particularly important for efficient charge extraction. Although cadmium-free electron transport layers such as TiO_2 , SnO_2 , and ZnO are actively being explored, the best-performing devices reported so far are still predominantly based on CdS, demonstrating that interface optimization, defect control, and microstructural engineering remain closely intertwined challenges. SnS solar cells occupy a less mature but scientifically instructive position. CdS has provided the benchmark heterojunction, but device performance is still limited by intrinsic defects and interfacial recombination. Alternative buffers such as Zn(O,S), $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, and ZnSnO demonstrate that engineering the conduction band mismatch can improve selectivity, where lower S/Zn ratios establish the ideal small positive spike, whereas higher sulfur fractions shift the band edge to values that severely block majority carriers [99]. Although efficiencies remain modest compared to more established thin-film absorbers. At the same time, the emergence of n-type SnS and p-SnS/n-SnS homojunction concepts suggests that future advances could involve not only replacing CdS but also

redesigning the junction architecture itself. Iron pyrite, FeS_2 , represents a fundamentally different case. Despite its attractive optical properties, including a narrow band gap, high absorption coefficient, and naturally abundant composition, photovoltaic performance remains severely limited by intrinsic surface and bulk electronic defects. Sulfur vacancies, deep donor states, and Fermi-level pinning suppress V_{oc} and can promote surface inversion, short-circuiting the junction rendering buffer layer optimization largely ineffective. The comparison presented in Figure 5 highlights that the effectiveness of CdS replacement is strongly absorber-dependent and can be broadly classified into three categories according to the dominant performance-limiting mechanisms. The first includes absorber systems such as CdTe/CdSeTe and CIGS, where front-interface recombination and band alignment represent the principal challenges and can be effectively addressed through front-interface engineering. The other four comprise CZTS/CZTSSe, $\text{Sb}_2(\text{S,Se})_3$, Sb_2Se_3 and SnS absorbers, in which both interface-related losses and bulk defects contribute significantly to the overall performance limitation, requiring simultaneous optimization of absorber quality and junction design. Finally, FeS_2 represents the limiting case where intrinsic surface and bulk electronic defects dominate device behavior, making buffer layer replacement alone insufficient to achieve substantial efficiency improvements.

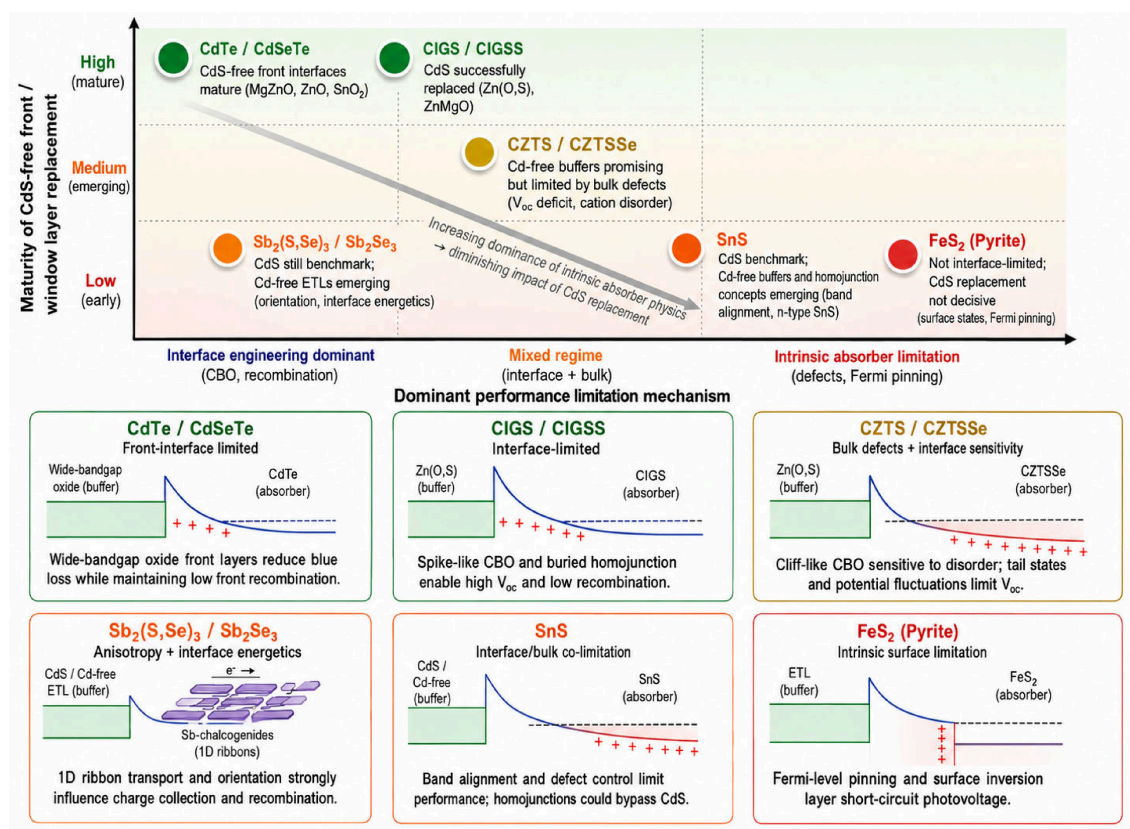


Figure 5. Schematic comparison of CdS-replacement maturity and dominant performance-limiting mechanisms in different thin-film absorber families. CdTe/Cd(Se,Te) and CIGS represent the most mature cases for CdS-free front-interface engineering, while kesterites, antimony chalcogenides and SnS remain limited by combined interface and absorber-related losses. FeS_2 represents the limiting case where intrinsic surface and bulk electronic defects make buffer-layer replacement secondary. This conceptual schematic was originally prepared by the authors. The position of each absorber family reflects the relative importance of front-interface engineering and intrinsic absorber limitations, ranging from systems mainly limited by front-interface recombination and band alignment to those dominated by intrinsic absorber defects.

9. Conclusions

The long-standing success of CdS in thin-film photovoltaics arises from the combination of multiple optical, electronic and chemical functions, including favorable junction formation, suitable band alignment, interfacial passivation, chemical compatibility and process robustness. Consequently, replacing CdS cannot be regarded as the simple substitution of one material by another, but rather as the reconstruction of the multifunctional role that CdS has historically played at the front interface. As discussed throughout this review, the feasibility of CdS replacement is strongly absorber-dependent. CdS-free architectures have already demonstrated technological maturity when optical losses and front-interface recombination are the dominant limitations, whereas systems limited by bulk disorder, metastability, unfavorable defect chemistry or surface electronic instability require broader materials and interface optimization beyond buffer-layer replacement alone. Future progress will therefore rely on predictive absorber-specific interface engineering rather than empirical buffer substitution. Compositionally tuneable oxides and chalcogenides, atomic-scale passivation, controlled interdiffusion and scalable low-damage deposition processes are expected to play a central role in developing front interfaces that simultaneously provide optimized band alignment, defect passivation, optical transparency, chemical stability and manufacturability. In this perspective, the transition beyond CdS should be viewed not simply as the replacement of a conventional material, but as the development of absorber-specific junction architectures capable of delivering higher efficiency together with improved sustainability.

Author Contributions: Conceptualization, A.B. and S.P.; Validation, A.B.; Writing—original draft, S.P. and A.B.; Writing—review & editing, S.P., A.B., S.R. and M.K.; Supervision A.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

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

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