

# Grain Engineering of $\text{Sb}_2\text{S}_3$ Thin Films to Enable Efficient Planar Solar Cells with High Open-Circuit Voltage

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$\text{Sb}_2\text{S}_3$  is a promising environmentally friendly semiconductor for high performance solar cells. But, like many other polycrystalline materials,  $\text{Sb}_2\text{S}_3$  is limited by nonradiative recombination and carrier scattering by grain boundaries (GBs). This work shows how the GB density in  $\text{Sb}_2\text{S}_3$  films can be significantly reduced from  $1068 \pm 40$  to  $327 \pm 23 \text{ nm } \mu\text{m}^{-2}$  by incorporating an appropriate amount of  $\text{Ce}^{3+}$  into the precursor solution for  $\text{Sb}_2\text{S}_3$  deposition. Through extensive characterization of structural, morphological, and optoelectronic properties, complemented with computations, it is revealed that a critical factor is the formation of an ultrathin  $\text{Ce}_2\text{S}_3$  layer at the  $\text{CdS}/\text{Sb}_2\text{S}_3$  interface, which can reduce the interfacial energy and increase the adhesion work between  $\text{Sb}_2\text{S}_3$  and the substrate to encourage heterogeneous nucleation of  $\text{Sb}_2\text{S}_3$ , as well as promote lateral grain growth. Through reductions in nonradiative recombination at GBs and/or the  $\text{CdS}/\text{Sb}_2\text{S}_3$  heterointerface, as well as improved charge-carrier transport properties at the heterojunction, this work achieves high performance  $\text{Sb}_2\text{S}_3$  solar cells with a power conversion efficiency reaching 7.66%. An impressive open-circuit voltage ( $V_{\text{OC}}$ ) of 796 mV is achieved, which is the highest reported thus far for  $\text{Sb}_2\text{S}_3$  solar cells. This work provides a strategy to simultaneously regulate the nucleation and growth of  $\text{Sb}_2\text{S}_3$  absorber films for enhanced device performance.

## 1. Introduction


Antimony chalcogenides have emerged as promising light-harvesting materials for next-generation photovoltaic devices in recent years.<sup>[1]</sup> This V-VI system, mainly including  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{Se}_3$ , and  $\text{Sb}_2(\text{S,Se})_3$ , has drawn increasing attention owing to its highly desirable features and properties, such as its composition of earth-abundant and environmentally benign elements, high thermal and environmental stability, simple binary composition, high visible light absorption coefficients ( $10^4$ – $10^5 \text{ cm}^{-1}$ ), and tunable bandgaps ranging from 1.10 to 1.70 eV.<sup>[1b,c,2]</sup> Following many efforts by a growing community of researchers working on these systems, the record power conversion efficiencies (PCEs) of  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{Se}_3$ , and  $\text{Sb}_2(\text{S,Se})_3$  solar cells have reached 8.00%, 10.57%, and 10.75%, respectively.<sup>[1a,d,3]</sup> Particularly,  $\text{Sb}_2\text{S}_3$  has a bandgap of  $\approx 1.70 \text{ eV}$ , which is the optimal value for top-cells in monolithic tandem photovoltaics with silicon

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bottom cells, as well as for indoor photovoltaics.<sup>[4]</sup> The low melting points ( $\approx 500$  °C) and high vapor pressures enable the low-temperature fabrication of flexible and lightweight devices for powering Internet of Things devices.<sup>[4b,5]</sup> According to the detailed balance limit for single p-n junctions, the maximum photovoltaic performance parameters of absorbers with a 1.70 eV bandgap are an open-circuit voltage ( $V_{OC}$ ) of 1.402 V, a short-circuit current density ( $J_{SC}$ ) of 22.46 mA cm<sup>-2</sup>, a fill factor (FF) of 91%, and a PCE of 28.64%, under 1-sun AM 1.5G illumination.<sup>[5]</sup> However, although great performance improvements have been achieved recently, the record PCE of 8.00% for Sb<sub>2</sub>S<sub>3</sub> solar cells still lags far behind its radiative efficiency limit.<sup>[1a]</sup> The primary reason behind the poor efficiency is the low  $V_{OC}$ , which has stagnated to around 550–750 mV over the past decade. This represents a  $V_{OC}$  deficit (defined as  $E_g/q - V_{OC}$ ,  $E_g$  and  $q$  are the bandgap and the elementary charge, respectively) of >0.9 V, which exceeds those found in other solar absorbers with similar bandgaps, such as CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, GaAs, CdTe, etc.<sup>[5,6]</sup> Therefore, it is imperative to realize effective strategies to overcome the  $V_{OC}$  bottleneck of Sb<sub>2</sub>S<sub>3</sub> solar cells.

The large  $V_{OC}$  deficit in Sb<sub>2</sub>S<sub>3</sub> solar cells is generally attributed to the traps states in devices, which can occur at surfaces, in the bulk or at interfaces.<sup>[6b]</sup> First-principles calculations and experimental results have demonstrated that although Sb<sub>2</sub>S<sub>3</sub> is only a binary compound, the absorber film suffers from a complex defect chemistry, mainly from sulfur vacancies ( $V_S$ ), antimony vacancies ( $V_{Sb}$ ), Sb antisites ( $Sb_S$ ), and S antisites ( $S_{Sb}$ ).<sup>[7]</sup> These point defects, especially those with deep levels, could act as recombination centers, which would lower the quasi-Fermi level splitting and further decrease the  $V_{OC}$ . Another plausible explanation for the high  $V_{OC}$  deficit, proposed by Yang et al., is that it is due to the self-trapping of photoexcited charge-carriers, setting an upper limit in the maximum  $V_{OC}$  (to approximately 0.80 V) and PCE (to approximately 16.00%) for Sb<sub>2</sub>S<sub>3</sub> solar cells.<sup>[8]</sup> However, by investigating the electron-lattice interaction and theoretical limits of carrier mobility using first-principles and Boltzmann transport calculations, Wang et al. demonstrated band-like transport in Sb<sub>2</sub>S<sub>3</sub> and concluded that the key limiting factor is defect-trapping rather than self-trapping.<sup>[9]</sup> This suggests that the low photovoltage of Sb<sub>2</sub>S<sub>3</sub> solar cells could be surmountable with improved processing conditions to engineer the defect and interfacial properties of devices. This calls for further experimental efforts to mitigate the deleterious role of defects in Sb<sub>2</sub>S<sub>3</sub>.

For polycrystalline thin film-based optoelectronic devices, grain boundaries (GBs) significantly influence the optoelectronic properties of the semiconductor, and ultimately the device performance.<sup>[10]</sup> This is because GBs, where dangling or wrong bonds proliferate, would impede charge-carrier transport and increase the rate of nonradiative recombination. It has been widely suggested that Sb<sub>2</sub>S<sub>3</sub> has a quasi-1D crystal structure with [Sb<sub>4</sub>S<sub>6</sub>]<sub>n</sub> units bonded covalently together in the *c*-axis direction to form [Sb<sub>4</sub>S<sub>6</sub>]<sub>n</sub> ribbons.<sup>[11]</sup> Although this quasi-1D structure is suggested to enable nearly benign GBs in [001]-oriented grains, the Sb<sub>2</sub>S<sub>3</sub>-based devices would also inevitably involve the negative effects of GBs at the terminals of ribbons in polycrystalline films.<sup>[5]</sup> It is therefore critical to minimize the GB density in Sb<sub>2</sub>S<sub>3</sub> thin films to reduce nonradiative recombination losses.<sup>[12]</sup> Large, compact crystalline grains are also desirable to promote charge-carrier transport by minimizing their scattering

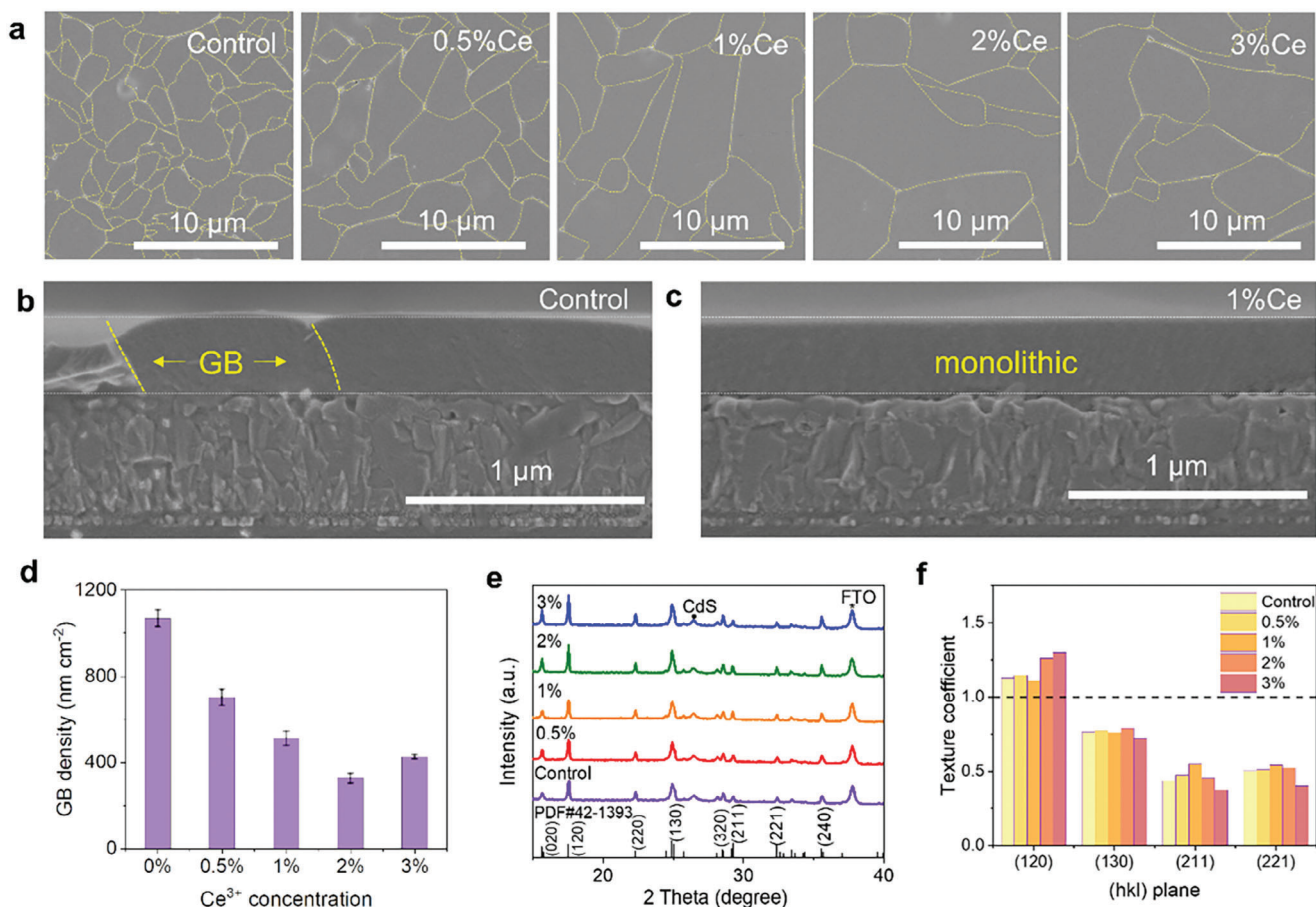
at GBs. However, grain growth is often quite difficult to control and poorly understood in Sb<sub>2</sub>S<sub>3</sub> absorbers. Conventional solution and evaporation processes and post-annealing approaches usually do not lead to large-grained compact thin films.<sup>[1a,2b,7b]</sup> To date, the great efforts to boost the performance of Sb<sub>2</sub>S<sub>3</sub> solar cells mainly focus on device structure optimization, orientation regulation, interface engineering, band tailoring, charge transport layer modification, etc.<sup>[6a,13]</sup> There are few works aiming to regulate the microstructure of Sb<sub>2</sub>S<sub>3</sub> films to increase the grain size. Since the microstructure of thin films greatly depends on the initial nucleation and growth, it is important to be able to rationally design and control the nucleation and growth processes of Sb<sub>2</sub>S<sub>3</sub>.<sup>[14]</sup> However, because of the complexity of the reactions involved in solution- and vapor-based systems, mechanisms of nucleation and growth remain obscure right now.<sup>[11,15]</sup> For example, for solution-based deposition, the adsorption and reaction of ions at the solid–liquid interface involve random processes, causing great difficulty in controlling the nucleation and growth of films.<sup>[16]</sup> Engineering the grains and the GB network to fabricate large-grained Sb<sub>2</sub>S<sub>3</sub> absorber films remains challenging.

The nucleation and growth of thin films are closely associated with the in situ chemical environment of precursors for deposition. Lanthanide ions have been successfully used to regulate the crystallization process and materials properties of semiconductors, such as CsPbBr<sub>3</sub> films and nanocrystals.<sup>[12a,17]</sup> Inspired by this fact, in this work, we investigated the incorporation of a variety of lanthanides (Ce<sup>3+</sup>, La<sup>3+</sup>, Gd<sup>3+</sup>, Yb<sup>3+</sup>, Er<sup>3+</sup>, and Tm<sup>3+</sup>) into the precursor solution for the hydrothermal deposition of Sb<sub>2</sub>S<sub>3</sub> films, and found that the addition of Ce<sup>3+</sup> allows effective grain engineering, which successfully resulted in large-grain Sb<sub>2</sub>S<sub>3</sub> absorber films with ultralow-density GB networks. Systematic characterization was performed to clarify the role of Ce<sup>3+</sup>, from which we propose that the formation of Ce<sub>2</sub>S<sub>3</sub> at the CdS/Sb<sub>2</sub>S<sub>3</sub> interface mediates nucleation and growth, leading to large-grained Sb<sub>2</sub>S<sub>3</sub> films at the solid–liquid interface. As expected, this near-ideal microstructure of large-grain Sb<sub>2</sub>S<sub>3</sub> films affords superior optoelectronic properties and significantly enhanced performance in planar heterojunction Sb<sub>2</sub>S<sub>3</sub> solar cells. A competitive PCE of 7.66% was achieved, coupled with a record  $V_{OC}$  value of 796 mV for the Sb<sub>2</sub>S<sub>3</sub> system. We performed a series of advanced measurements to understand in detail the effects of Ce<sup>3+</sup> addition on nonradiative recombination in the Sb<sub>2</sub>S<sub>3</sub> photovoltaic devices to rationalize the reasons behind the improvement in performance. This study therefore develops a novel method for tuning the grain size of Sb<sub>2</sub>S<sub>3</sub> thin films to realize high-performance photovoltaic devices.

## 2. Results and Discussion

### 2.1. Preparation of Large-Grained Sb<sub>2</sub>S<sub>3</sub> Thin Films

We employed the hydrothermal method to deposit Sb<sub>2</sub>S<sub>3</sub> absorber films on FTO/SnO<sub>2</sub>/CdS substrates, in which C<sub>4</sub>H<sub>4</sub>KO<sub>7</sub>Sb·0.5H<sub>2</sub>O and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O were used as Sb and S sources, respectively. An extra amount of extrinsic Ce-based salts were intentionally incorporated into the precursor solution. **Figure 1a** shows top-down scanning electron microscopy (SEM) images of Sb<sub>2</sub>S<sub>3</sub> thin films after 180 min of growth, prepared

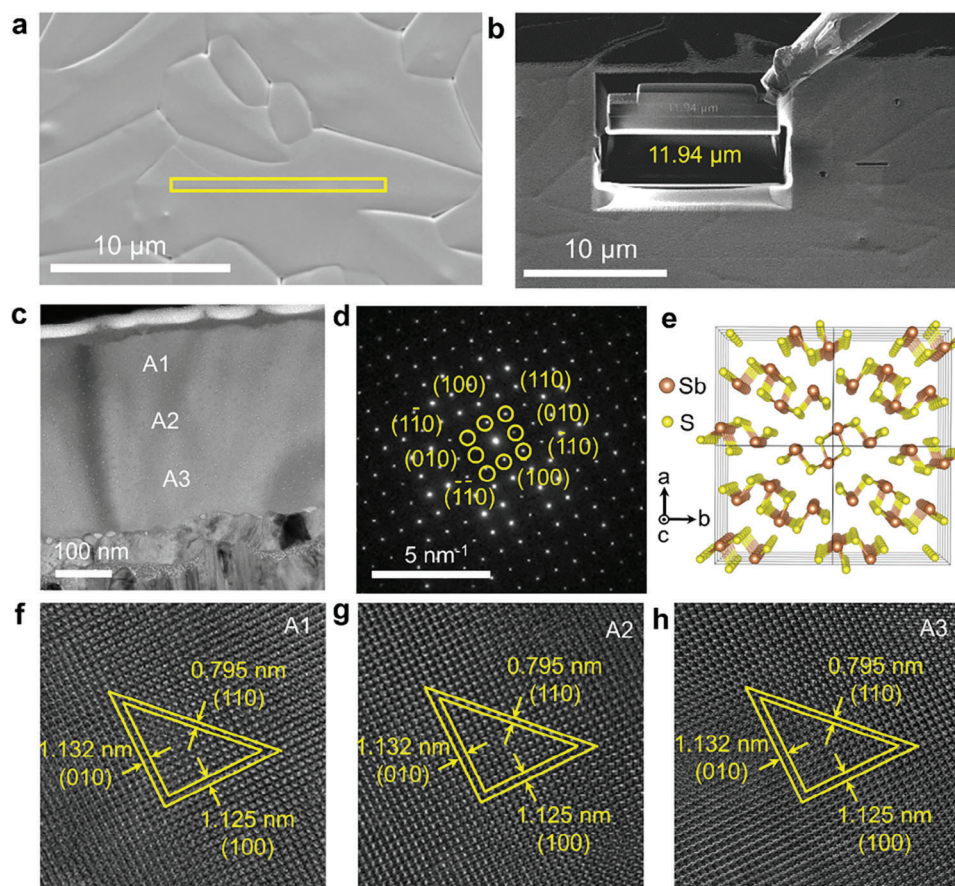


**Figure 1.** a) Top-view scanning electron microscopy (SEM) images of  $\text{Sb}_2\text{S}_3$  thin films prepared without (i.e., control) and with the addition of  $\text{Ce}(\text{CH}_3\text{COO})_3$  salt, with molar ratios of  $\text{Ce}^{3+}/\text{Sb}^{3+} = 0.5\%$ , 1%, 2%, and 3%. The hydrothermal deposition time was 180 min in all cases. The grain boundaries (GBs) are highlighted to show more clearly the changes in the GB density. b,c) Cross-sectional SEM images of the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  films. d) The dependence of the GB density on the  $\text{Ce}^{3+}$  concentration in the precursor solution. Three samples were measured to determine the mean GB density values shown, and the error bars represent the standard deviation. e) X-ray diffraction (XRD) patterns of the control  $\text{Sb}_2\text{S}_3$  film and Ce- $\text{Sb}_2\text{S}_3$  films prepared with different  $\text{Ce}^{3+}$  concentrations. f) Texture coefficients of the (120), (130), (211), and (221) peaks, which dominate the diffraction patterns of the  $\text{Sb}_2\text{S}_3$  films.

without (i.e., control) and with the addition of different amounts of  $\text{Ce}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$ . The molar ratio of  $\text{Ce}^{3+}/\text{Sb}^{3+}$  prepared in the precursor solution were 0.5%, 1%, 2% and 3%, and we hereinafter refer to the films prepared based on the ratios used in the precursor solution. As shown, the control  $\text{Sb}_2\text{S}_3$  film has a grain size of 2.5–5.0  $\mu\text{m}$  based on the characteristic diameters of grains, which is close to those reported in the literature.<sup>[11,15]</sup> The addition of  $\text{Ce}^{3+}$  into the precursor solution significantly increases the  $\text{Sb}_2\text{S}_3$  grain size. When the  $\text{Ce}^{3+}$  concentration reaches 1%–3%, a large number of grains exceed 10  $\mu\text{m}$  in size, with some grains even exceeding 15  $\mu\text{m}$ . The cross-sectional SEM images of control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$ , as given in Figure 1b,c, reveal that as-obtained  $\text{Sb}_2\text{S}_3$  grains span across the thickness of  $\approx 280$  nm absorber layers, which would facilitate efficient carrier transport between the charge transport layers.<sup>[10b]</sup> The addition of  $\text{Ce}^{3+}$  has negligible influence on the thickness of  $\text{Sb}_2\text{S}_3$  layers; however, the control  $\text{Sb}_2\text{S}_3$  film suffers from some vertical GBs while the 1%Ce- $\text{Sb}_2\text{S}_3$  sample affords monolithic grains. To further quantify the GB density, we defined it as the length of GBs per unit area, and calculated

the density of the GB network by first highlighting the GB grooves in top-down SEM images of  $\text{Sb}_2\text{S}_3$  films. As shown in Figure 1d, the GB density on the  $\text{Sb}_2\text{S}_3$  film surface is reduced from  $1068 \pm 40 \text{ nm } \mu\text{m}^{-2}$  for the control sample to  $702 \pm 37$ ,  $511 \pm 33$ ,  $327 \pm 23$ ,  $427 \pm 11 \text{ nm } \mu\text{m}^{-2}$  for the 0.5%, 1%, 2%, and 3%Ce- $\text{Sb}_2\text{S}_3$  film samples, respectively. That is, the addition of  $\text{Ce}^{3+}$  into the precursor solution enables the well-controlled evolution of large grains with ultra-low GB density.

X-ray diffraction (XRD) patterns of  $\text{Sb}_2\text{S}_3$  films without and with the addition of  $\text{Ce}^{3+}$  (Figure 1e) show the films prepared to be phase-pure, apart from peaks from the FTO substrate the films were deposited onto. The peaks from the absorber could all be indexed to orthorhombic  $\text{Sb}_2\text{S}_3$  with a space group of  $Pbnm$  (JCPDS #42-1393).<sup>[1a,5]</sup> The dominant peaks are (120), (220), (130), (211) and (211). By calculating the texture coefficients of these peaks, we found that the addition of  $\text{Ce}^{3+}$  does not cause significant changes to the degree of preferred orientation (Figure 1f). In addition, the diffraction peaks show no evident shift with the addition of  $\text{Ce}^{3+}$ , which suggests that  $\text{Ce}^{3+}$  is not incorporated into lattice or interstitial sites.



**Figure 2.** a,b) Scanning electron microscopy (SEM) images of the 1%Ce-Sb<sub>2</sub>S<sub>3</sub> film used for making samples for transmission electron microscopy (TEM) characterization, and corresponding process of obtaining the lamella using a focused ion beam. c) Cross-sectional TEM image of 1%Ce-Sb<sub>2</sub>S<sub>3</sub> sample deposited on FTO/SnO<sub>2</sub>/CdS substrate. d) Selected area electron diffraction (SAED) pattern from Sb<sub>2</sub>S<sub>3</sub> crystals, with diffraction spots indexed. e) Illustration of the crystal structure of Sb<sub>2</sub>S<sub>3</sub>, viewed from the [001] direction. f–h) High-resolution (HR) TEM measurements performed at points A1, A2, and A3 (see part c), and the corresponding lattice fringes.

By definition, a grain is the smallest microstructural unit that is a true single crystal and is bounded on all sides by GBs, interfaces, or surfaces.<sup>[14b]</sup> Since the microfeatures found from SEM images are not necessarily individual grains, we here further quantified this from transmission electron microscopy (TEM) measurements. **Figure 2a,b** shows SEM images of the 1%Ce-Sb<sub>2</sub>S<sub>3</sub> film used for making samples for TEM characterization and corresponding process of obtaining the lamella using a focused ion beam (FIB) system, respectively. The cross-sectional TEM image (Figure 2c) reveals that the Sb<sub>2</sub>S<sub>3</sub> film is compact and composed of large Sb<sub>2</sub>S<sub>3</sub> grains spanning the thickness of the film. To verify whether the Sb<sub>2</sub>S<sub>3</sub> grains are single crystalline, high-resolution TEM was used to analyze three arbitrarily selected points A1, A2, and A3 as labeled in Figure 2c, with the corresponding lattice fringes given in Figure 2f–h. As shown, lattice fringes with interplanar spacings of 1.132, 1.125, and 0.795 nm were identified, which corresponds to the (010), (100), and (110) planes in orthorhombic Sb<sub>2</sub>S<sub>3</sub>, respectively.<sup>[5]</sup> Points A1, A2, and A3 have identical crystallographic orientations, reflecting that the crystal planes extend from the top to the bottom of the Sb<sub>2</sub>S<sub>3</sub> film. This confirms that the large grain is indeed single crystalline. The selected-area electron diffraction (SAED) pattern (Figure 2d),

which is observed from the [001] zone axis as illustrated by the atomic configuration of ribbon direction [001] orientation in the Sb<sub>2</sub>S<sub>3</sub> crystal structure (Figure 2e), further confirms the single-crystalline nature of the Sb<sub>2</sub>S<sub>3</sub> grains.

Atomic force microscopy (AFM) measurements (Figure S1, Supporting Information) further reveal that the 1%Ce-Sb<sub>2</sub>S<sub>3</sub> sample displays much larger microfeatures than the control Sb<sub>2</sub>S<sub>3</sub> sample. Moreover, the addition of Ce<sup>3+</sup> results in a reduction in the average roughness of the absorber films from 13.1 nm (control) to 9.2 nm (1%Ce-Sb<sub>2</sub>S<sub>3</sub>). Flatter and more compact absorber films would enable the formation of high-quality P-N junctions. The conductive-atomic force microscopy (c-AFM) images and corresponding height profile and current analysis of the control Sb<sub>2</sub>S<sub>3</sub> and 1%Ce-Sb<sub>2</sub>S<sub>3</sub> films are provided in Figure S2a–d (Supporting Information). The intensity profiling of the surface current along the solid white line marked in Figure S2a–b (Supporting Information) reveals that the films suffer from evident current fluctuations at the GBs. The 1%Ce-Sb<sub>2</sub>S<sub>3</sub> films have more homogeneous and slightly increased electrical conductivity across the 5 μm scale compared to the control film. The reduced fluctuation in the current intensity for 1%Ce-Sb<sub>2</sub>S<sub>3</sub> films favors local photocurrent generation and collection,

effectively suppressing carrier recombination at the GBs.<sup>[18]</sup> The Fermi level, valence band (VB) and conduction band (CB) of the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  films can be derived from ultraviolet photoelectron spectroscopy (UPS) measurements (Figure S3a, Supporting Information; see details in Note S2, Supporting Information). A schematic diagram of the band positions of the functional layers in  $\text{Sb}_2\text{S}_3$  solar cells is illustrated in Figure S3b (Supporting Information).<sup>[19]</sup> As shown, the Fermi level of the 1%Ce- $\text{Sb}_2\text{S}_3$  film is shifted up towards the CB compared to that of the control  $\text{Sb}_2\text{S}_3$  film. The lower work function (WF) implies an increased electron carrier concentration, and therefore more n-type  $\text{Sb}_2\text{S}_3$ . We further performed Kelvin probe force microscopy (KPFM) measurements to map the surface potential of  $\text{Sb}_2\text{S}_3$  films, as shown in Figure S2e–h (Supporting Information), which reveal a higher surface potential for the 1%Ce- $\text{Sb}_2\text{S}_3$  film in contrast to the control  $\text{Sb}_2\text{S}_3$ . An increased surface potential indicates a lower WF.<sup>[18,20]</sup> Therefore, the WF value of the 1%Ce- $\text{Sb}_2\text{S}_3$  sample would be lower than that of the control sample, implying the upshift of the Fermi levels as a result of increased background electron concentration.<sup>[21]</sup> To evaluate the conductivity of the absorber films, we measured the  $I$ – $V$  curves in the dark based on a simple device configuration of FTO/ $\text{Sb}_2\text{S}_3$ /Au for the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  film samples (Figure S4, Supporting Information). The 1%Ce- $\text{Sb}_2\text{S}_3$  film delivers an enhanced conductivity of  $7.50 \times 10^{-5} \text{ S cm}^{-1}$ , higher than that of  $4.32 \times 10^{-5} \text{ S cm}^{-1}$  for the control film, and this is consistent with the c-AFM results. Since the conductivity measurement here is out-of-plane and most of the GBs in  $\text{Sb}_2\text{S}_3$  films are approximately vertical, the increase in conductivity  $\sigma$  reflects the increase of electron density according to the equation  $\sigma = ne\mu_e$ , where  $n$  is the electron concentration,  $e$  is the elementary charge, and  $\mu_e$  is the electron mobility.

Finally, in addition to  $\text{Ce}^{3+}$ , we also investigated other lanthanide additives ( $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Tm}^{3+}$ ). However, the addition of these ions into the precursor solution did not lead to the changes in microstructure obtained with  $\text{Ce}^{3+}$ , as shown by the SEM images and corresponding photovoltaic device performances given in Figure S5 and Table S1 (Supporting Information).

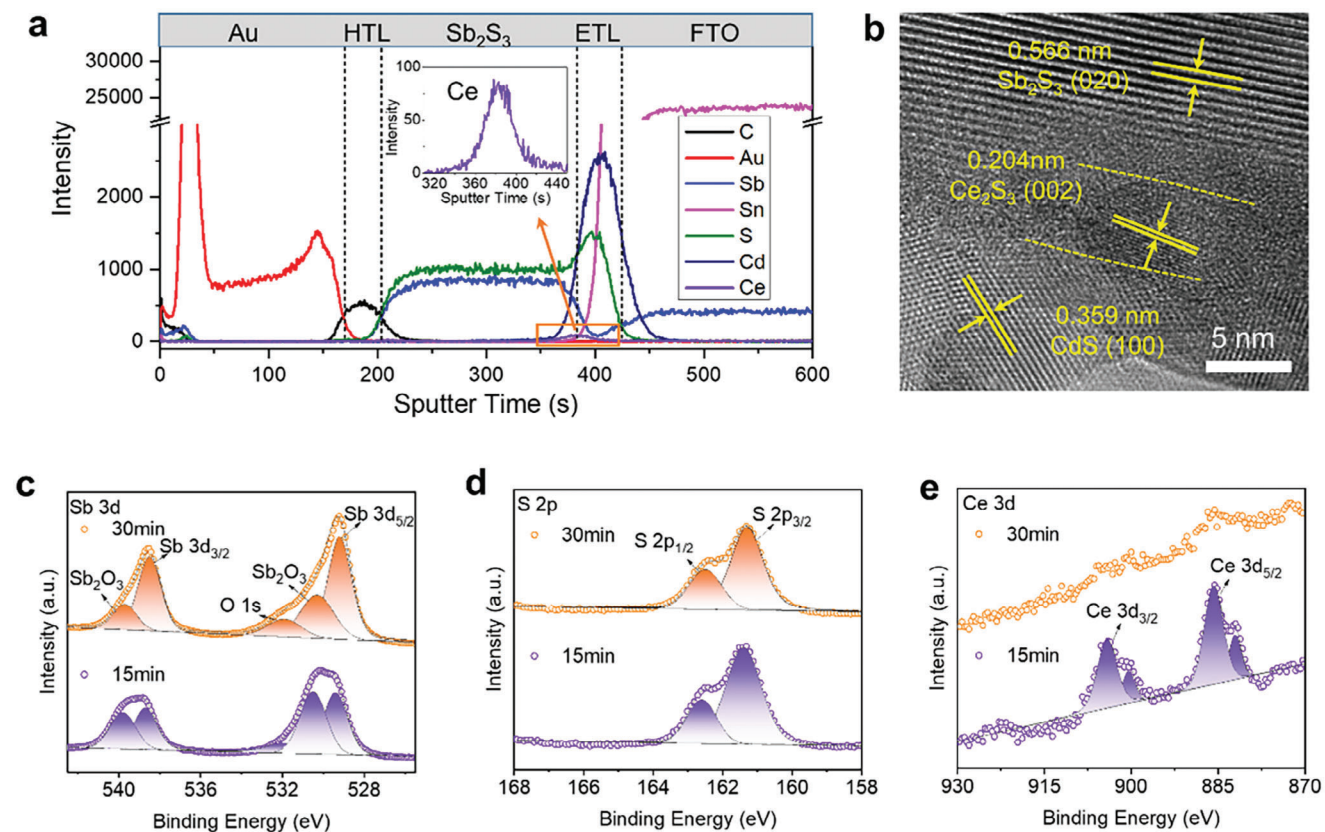
## 2.2. Growth Mechanism of Large-Grained $\text{Sb}_2\text{S}_3$ Films

To elucidate the underlying mechanism for the increase in  $\text{Sb}_2\text{S}_3$  grain size, we performed control experiments as follows. Apart from using  $\text{Ce}(\text{CH}_3\text{COO})_3$  as the additive into the precursor solution, we investigated the use of Ce-based salts of  $\text{CeCl}_3$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , which were also found to be effective in promoting the grain size of  $\text{Sb}_2\text{S}_3$  film, as reflected in the SEM images shown in Figure S6a,b (Supporting Information). In addition, we found that adding 1% molar ratio  $\text{Ce}(\text{CH}_3\text{COO})_3$  to the precursor solution for hydrothermal deposition would slightly increase the pH from 4.38 to 4.73. In order to exclude the influence of pH, we further used ammonia solution to adjust the pH of the precursor solution without the additive of  $\text{Ce}^{3+}$  to a similar level of 1%  $\text{Ce}(\text{CH}_3\text{COO})_3$  containing precursor, as summarized in Table S2 (Supporting Information). After examining the grain size of as-prepared  $\text{Sb}_2\text{S}_3$  films with the addition of ammonia solution (Figure S6c, Supporting Information), we found that changing

pH has negligible influence on the grain size of  $\text{Sb}_2\text{S}_3$ . These results confirm that the increase in  $\text{Sb}_2\text{S}_3$  grain size should be closely associated with the presence of  $\text{Ce}^{3+}$  in the precursor solution. In this work, we employed  $\text{Ce}(\text{CH}_3\text{COO})_3$  as the Ce-salt additive incorporated into the precursor solutions, unless otherwise stated.

Next, we clarified the specific effects of  $\text{Ce}^{3+}$  on the growth of  $\text{Sb}_2\text{S}_3$  films and corresponding device performance. Generally, extrinsic  $\text{Ce}^{3+}$  ions could be incorporated into the crystal lattice of  $\text{Sb}_2\text{S}_3$  (i.e., doping) or concentrate at GBs or interfaces. Aiming to determine the exact location of  $\text{Ce}^{3+}$ , we performed secondary ion mass spectrometry (SIMS) measurements to analyze the vertical distribution of various elements across the 1%Ce- $\text{Sb}_2\text{S}_3$  film. The SIMS intensity profiles of C, Au, Sb, Sn, S, Cd, and Ce in FTO/ $\text{SnO}_2$ / $\text{CdS}/\text{Sb}_2\text{S}_3$ /Spiro-OMeTAD/Au are shown in Figure 3a. Herein, we used  $^{110}\text{Cd}$  and  $^{142}\text{Ce}$  isotopes to avoid interference from other ions on identifying these elements. It is revealed that Sb and S distribute uniformly across the absorber layer ( $t = 205$ – $385 \text{ s}$ ). At the  $\text{CdS}/\text{Sb}_2\text{S}_3$  heterojunction interface ( $t = 385 \text{ s}$ ), an abrupt increase in the Ce profile peak was clearly observed, suggesting the accumulation of Ce-based compounds at the  $\text{CdS}/\text{Sb}_2\text{S}_3$  interface. We speculate that the  $\text{Ce}^{3+}$  incorporated probably reacted with S-species in the precursor solution to generate  $\text{Ce}_2\text{S}_3$  compounds on top of the pristine  $\text{CdS}$  layer. Moreover, the symmetric distribution of the Ce peak also excludes the possible gradient doping of  $\text{Ce}^{3+}$  into  $\text{Sb}_2\text{S}_3$ . The 3D-SIMS mapping images of Sb, Cd, Ce, and S elements (Figure S7, Supporting Information) further reflect that the location of Ce element at the  $\text{CdS}/\text{Sb}_2\text{S}_3$  interface.

Figure 3b presents the HRTEM image at the  $\text{CdS}/\text{Sb}_2\text{S}_3$  interface of the 180 min-deposited 1%Ce- $\text{Sb}_2\text{S}_3$  thin film, which reveals there to be an ultrathin interlayer. This interlayer has lattice fringes with the interplanar spacing of  $\approx 0.204 \text{ nm}$ , corresponding to the (002) plane of orthorhombic  $\text{Ce}_2\text{S}_3$  (space group Pnam). X-ray photoelectron spectroscopy (XPS) was also performed to confirm the formation of  $\text{Ce}_2\text{S}_3$  at the  $\text{CdS}/\text{Sb}_2\text{S}_3$  interface. Here, in order to successfully characterize the  $\text{CdS}/\text{Sb}_2\text{S}_3$  interface, we fabricated ultrathin 1%Ce- $\text{Sb}_2\text{S}_3$  film samples prepared with 15 min- and 30 min of hydrothermal deposition. These film samples were not etched by  $\text{Ar}^+$  sputtering because of the limited amount of cerium compounds on the film surface. As shown in Figure 3c, the binding energies (BEs) of 538.5 and 529.2 eV are assigned to the  $\text{Sb } 3d_{3/2}$  and  $\text{Sb } 3d_{5/2}$  core levels of  $\text{Sb}_2\text{S}_3$ , respectively, while the peaks centered at 539.7 and 530.4 eV are ascribed to  $\text{Sb}_2\text{O}_3$ , probably arising from the partial post-oxidation of the film surface in air.<sup>[22]</sup> The BEs of  $\text{S } 2p_{1/2}$  and  $\text{S } 2p_{3/2}$  for both film samples are 162.6 and 161.4 eV, respectively (Figure 3d).<sup>[23]</sup> Figure 3e shows characteristic peaks of high-resolution Ce 3d, which presents two pairs of spin-orbit signals. The peaks located at 904.2 and 885.5 eV can be attributed to Ce  $3d_{3/2}$  and Ce  $3d_{5/2}$  for the  $\text{Ce}^{3+}$  state in  $\text{Ce}_2\text{S}_3$ , respectively. The other pair of peaks at 900.5 and 882.4 eV is assigned to the satellite peak of  $\text{Ce}^{3+}$ . The results are consistent with those reported in the literature for  $\text{Ce}_2\text{S}_3$ , indicating the existence of  $\text{Ce}^{3+}$ .<sup>[24]</sup> Moreover, the reduced Ce peak intensity for the 30 min-deposited film compared to the 15 min-deposited film as well as the quantitative analysis of atomic ratios further implies the preferential formation of  $\text{Ce}_2\text{S}_3$  prior to the deposition of  $\text{Sb}_2\text{S}_3$  (Table S3, Supporting Information). High resolution XPS spectra and spectral



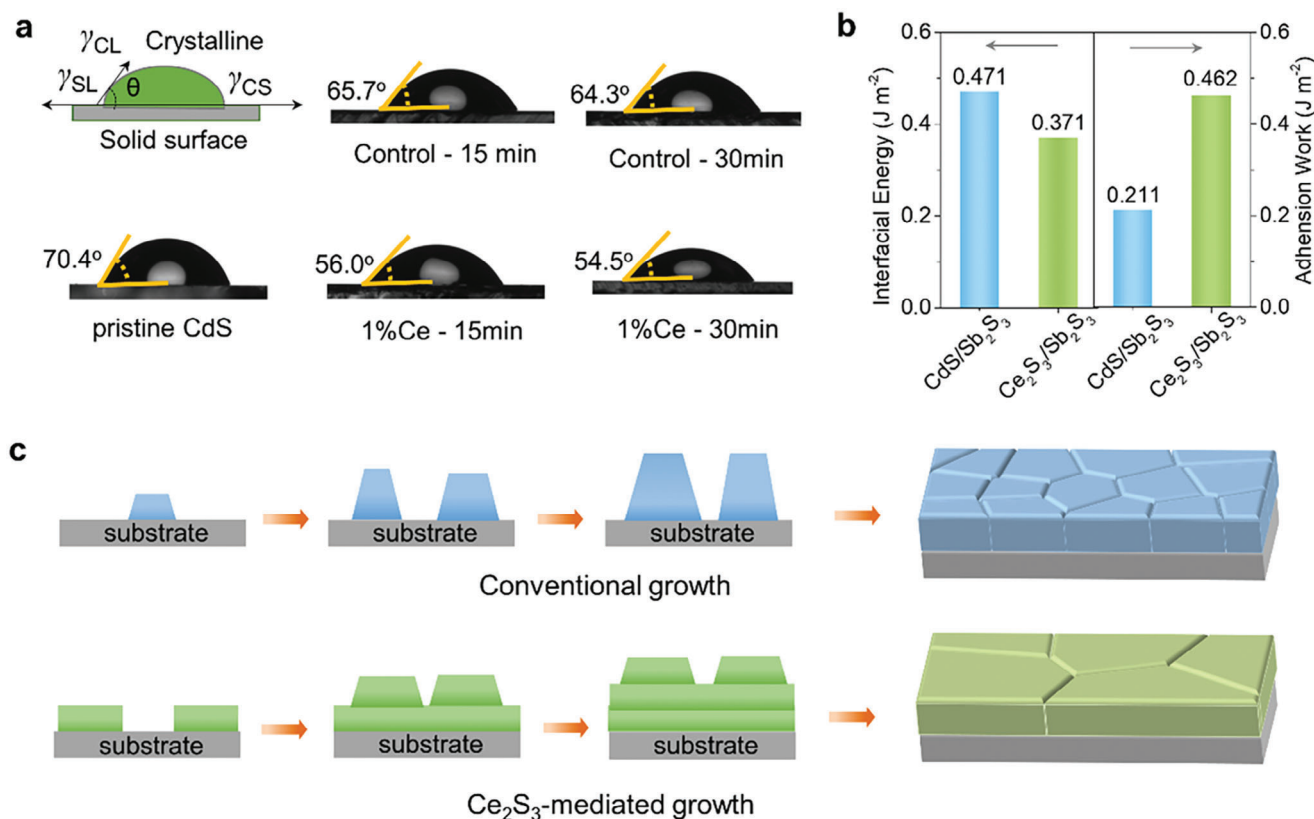
**Figure 3.** a) Secondary ion mass spectrometry (SIMS) depth profiles of the 180 min-deposited 1%Ce-Sb<sub>2</sub>S<sub>3</sub> thin film. b) HRTEM image at the CdS/Sb<sub>2</sub>S<sub>3</sub> interface of the 180 min-deposited 1%Ce-Sb<sub>2</sub>S<sub>3</sub> thin film. c–e) High resolution X-ray photoelectron spectroscopy (XPS) spectra of Sb 3d, S 2p, and Ce 3d core levels, along with peaks fitted to these spectra, for the 15 min- and 30 min-deposited 1%Ce-Sb<sub>2</sub>S<sub>3</sub> film samples.

deconvolution analysis of Sb 3d, S 2p, and Ce 3d for 180 min-deposited control Sb<sub>2</sub>S<sub>3</sub> and 1%Ce-Sb<sub>2</sub>S<sub>3</sub> film samples are given in Figure S8 (Supporting Information). The failure to detect the Ce 3d peak implies the absence of Ce elements at the surface of Sb<sub>2</sub>S<sub>3</sub> and excludes the uniform doping or distribution of Ce in the bulk Sb<sub>2</sub>S<sub>3</sub> film.

To gain more insights into the evolution of the morphology with Ce<sup>3+</sup> incorporation, we performed SEM measurements at different time intervals during film growth. Figure S9 (Supporting Information) shows top-down and cross-sectional view SEM images of the control Sb<sub>2</sub>S<sub>3</sub> and 1%Ce-Sb<sub>2</sub>S<sub>3</sub> film samples prepared with different deposition durations (15, 30, 60, 120, and 180 min) by hydrothermal growth. A comparison of the morphology of the control and 1%Ce-Sb<sub>2</sub>S<sub>3</sub> films prepared with identical deposition times reveals that the addition of Ce<sup>3+</sup> results in an increase in the grain size of Sb<sub>2</sub>S<sub>3</sub> over the course of the entire deposition process sampled. Moreover, it seems to be difficult to deposit Sb<sub>2</sub>S<sub>3</sub> onto pristine CdS at the initial stage of hydrothermal deposition (0–30 min). In contrast, when Ce<sup>3+</sup> was incorporated, an evident film morphology change occurs for the 30 min-deposited sample, probably resulting from the preferential deposition of Ce<sub>2</sub>S<sub>3</sub>. Another interesting phenomenon is that the addition of Ce<sup>3+</sup> also reduces the amount of white precipitate particles on the surface of Sb<sub>2</sub>S<sub>3</sub> films, which may be due to suppressed homogeneous nucleation that occurs in hydrothermal solutions.<sup>[16c]</sup> In addition to measuring the morphology by top-

down SEM, we also measured the cross-section of these samples, and found that there was no distinct difference in the thickness of the Sb<sub>2</sub>S<sub>3</sub> absorbers without or with the addition of Ce<sup>3+</sup> (Figure S9c,d, Supporting Information).

Taken together, the TEM, XRD, SIMS, and XPS results exclude the possibility of substitutional or interstitial doping of Ce<sup>3+</sup> in the Sb<sub>2</sub>S<sub>3</sub> host. Aiming to determine the complicated film growth route of hydrothermal deposition, it is worth noting that the overall reaction is a joint result of kinetic and thermodynamic processes. Although the Sb<sup>3+</sup>, Ce<sup>3+</sup>, and S<sup>2-</sup> sources were simultaneously dissolved into the precursor solution, different ions have quite different release rates. S<sup>2-</sup> ions are easily released from sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) upon hydrolytic decomposition. In contrast, considering the strong complexation effect of [Sb<sub>2</sub>(C<sub>4</sub>H<sub>2</sub>O<sub>6</sub>)<sub>2</sub>]<sup>2-</sup>, Sb<sup>3+</sup> ions in the precursor solution involve quite slow ion release rates, especially at the very beginning of the reaction period. Generally, the deposition of Sb<sub>2</sub>S<sub>3</sub> occurs when the ionic product (IP = [Sb<sup>3+</sup>]<sup>2</sup>[S<sup>2-</sup>]<sup>3</sup>) exceeds the solubility product of Sb<sub>2</sub>S<sub>3</sub> (K<sub>sp</sub> = 10<sup>-92.77</sup>).<sup>[25]</sup> Different from the complexation of [Sb<sub>2</sub>(C<sub>4</sub>H<sub>2</sub>O<sub>6</sub>)<sub>2</sub>]<sup>2-</sup>, the incorporated Ce-based salts can completely dissociate into free Ce<sup>3+</sup> ions in the growth medium. That is, Ce<sup>3+</sup> would be the dominating free cations available that could react with S<sup>2-</sup> during the initial reaction stage, enabling the higher nucleation and deposition rate for Ce<sub>2</sub>S<sub>3</sub>. Meanwhile, Ce<sup>3+</sup> is more active compared to Sb<sup>3+</sup> reacting with S<sup>2-</sup>, and thus the formation of Ce<sub>2</sub>S<sub>3</sub> dominates the initial reactions during the



**Figure 4.** a) Illustration of the contact angle ( $\theta$ ) for heterogeneous nucleation, and the water contact angles of pristine CdS film, as well as CdS films that have undergone 15 min- and 30 min-hydrothermal deposition in Sb<sub>2</sub>S<sub>3</sub> precursor solutions (both without and with 1% Ce). b) Histogram of the calculated interfacial adhesion work and interfacial energy for the heterointerfaces of CdS/Sb<sub>2</sub>S<sub>3</sub> and Ce<sub>2</sub>S<sub>3</sub>/Sb<sub>2</sub>S<sub>3</sub>. c) Schematic illustrating conventional growth and Ce<sub>2</sub>S<sub>3</sub>-mediated growth of Sb<sub>2</sub>S<sub>3</sub> thin films.

hydrothermal process. This can also be validated by the much lower formation energy of Ce<sub>2</sub>S<sub>3</sub> (−1.99 eV atom<sup>−1</sup>) compared to that of Sb<sub>2</sub>S<sub>3</sub> (−0.27 eV atom<sup>−1</sup>), as summarized in Table S4 (Supporting Information). Moreover, the limited supply of incorporated Ce<sup>3+</sup> ions would only result in the formation of an ultrathin layer of Ce<sub>2</sub>S<sub>3</sub> on top of the CdS layer, followed by a slow deposition of the Sb<sub>2</sub>S<sub>3</sub> absorber layer. From the perspective of crystal growth, the deposition of Sb<sub>2</sub>S<sub>3</sub> on the substrate is greatly influenced by the substrate characteristics, including chemical bonding environment and exposed crystal facets. We speculate that the pre-deposited Ce<sub>2</sub>S<sub>3</sub> seeds succeed in modifying the initial nucleation environment of Sb<sub>2</sub>S<sub>3</sub>. Herein we can apply materials science principles of nucleation and growth to understand the microstructural evolution of Sb<sub>2</sub>S<sub>3</sub> films and then propose a plausible mechanism.<sup>[14,26]</sup> The corresponding detailed descriptions of nucleation and growth are given in Note S1 (Supporting Information).

First, we measured the contact angle of water on the substrates used for Sb<sub>2</sub>S<sub>3</sub> deposition to understand the specific role of the Ce<sub>2</sub>S<sub>3</sub> interlayer on the nucleation behavior of Sb<sub>2</sub>S<sub>3</sub>. The interfacial energy diagram for two solids and a liquid in contact with each other is shown in Figure 4a, as well as the contact angle results of the pristine CdS film and the Sb<sub>2</sub>S<sub>3</sub> films after 15 min- and 30 min- hydrothermal deposition with and without Ce<sup>3+</sup>. Here  $\gamma_{CL}$ ,  $\gamma_{SL}$ , and  $\gamma_{CS}$  denote the interfacial en-

ergies between the crystalline phase and the liquid, the substrate and the liquid, and the crystalline phase and the solid surface, respectively. As shown, the water contact angle of the pristine CdS film is as high as 70.4°, which is slightly lowered to 65.7° and 64.3° for the films processed by 15 min- and 30 min-deposition without the use of Ce<sup>3+</sup>, respectively. On the other hand, adding Ce<sup>3+</sup> into the precursor solution dramatically reduces the water contact angle to 56° and 54.5° for 15 min- and 30 min-deposited samples, respectively. Since we have concluded that Ce<sub>2</sub>S<sub>3</sub> seeds would be preferentially deposited via 15 min- and 30 min-hydrothermal deposition, it is evident that the substrate becomes more hydrophilic with the presence of an ultrathin Ce<sub>2</sub>S<sub>3</sub> interlayer. Therefore, according to Equations (S1–S4) and Figure S10 (Supporting Information), during the nucleation stage, we suggest that the Ce<sub>2</sub>S<sub>3</sub> interlayer promotes the heterogeneous nucleation of Sb<sub>2</sub>S<sub>3</sub>, while suppressing its homogeneous nucleation. This is because smaller contact angle results in a reduced energy barrier for heterogeneous nucleation. This scenario is similar to the case for perovskite films, which generally require a high density of heterogeneous nuclei on the substrate to afford uniform, full-coverage thin films.<sup>[27]</sup>

Subsequently, stable Sb<sub>2</sub>S<sub>3</sub> nuclei will further grow to reduce the overall free energy of the system as long as the solute concentration is above the solubility limit. Typically, the growth of Sb<sub>2</sub>S<sub>3</sub> films occurs by a process akin to the Volmer-Weber growth

model (island), where the interface energy is relatively large, and hence discrete nuclei form and grow before a layer is completed by infilling. Here the 3D nuclei (i.e., islands) first grow both vertically and laterally onto the CdS substrate, and then form a dense polycrystalline film.<sup>[14]</sup> For the case where a Ce<sub>2</sub>S<sub>3</sub> interlayer is present, the growth of Sb<sub>2</sub>S<sub>3</sub> films more closely resembles the Stranski–Krastanov model (layer plus island), where the interface energy is comparable to the island interaction energy, and hence layer formation competes with nuclei formation. Here, high-density small nuclei formed on the CdS/Ce<sub>2</sub>S<sub>3</sub> substrate would tend more to grow laterally, which contrast to growth on the CdS substrate, and thus further coalesce into a large-grained Sb<sub>2</sub>S<sub>3</sub> film. This hypothesis is further supported by first-principles calculations, which reveals decreased interfacial energy ( $\gamma$ ) and increased adhesion work ( $W_{ad}$ ) for the Ce<sub>2</sub>S<sub>3</sub>/Sb<sub>2</sub>S<sub>3</sub> heterointerface compared to the CdS/Sb<sub>2</sub>S<sub>3</sub> heterointerface. Interfacial energy and adhesion work are two important parameters to evaluate the properties of the heterointerface. The interfacial energy can be regarded as the resistance to form an interface structure; heterointerfaces with smaller  $\gamma$  are easier to form. Adhesion work, which is defined as the work required to separate two phases from each other (herein the film and the substrate), can be used to evaluate the bond strength of interfaces. Generally, a larger  $W_{ad}$  implies a stronger heterointerface stability. Here we built CdS/Sb<sub>2</sub>S<sub>3</sub> and Ce<sub>2</sub>S<sub>3</sub>/Sb<sub>2</sub>S<sub>3</sub> heterojunction models by selecting CdS (100), Sb<sub>2</sub>S<sub>3</sub> (120), and Ce<sub>2</sub>S<sub>3</sub> (001) surfaces as exposed surfaces. Table S5 (Supporting Information) gives the calculated surface energies of various crystal surfaces, and the calculated interfacial energy and adhesion work of two heterointerface are shown in Figure 4b. We can see that the interfacial energy of the Ce<sub>2</sub>S<sub>3</sub>/Sb<sub>2</sub>S<sub>3</sub> heterointerface is 0.3705 J m<sup>-2</sup>, lower than that of 0.4709 J m<sup>-2</sup> for the CdS/Sb<sub>2</sub>S<sub>3</sub> heterointerface. This suggests that the nucleation and growth of Sb<sub>2</sub>S<sub>3</sub> on Ce<sub>2</sub>S<sub>3</sub> is easier to occur. The reduced interfacial energy and enhanced bonding at the substrate/absorber interface might promote the transition of the growth mode of Sb<sub>2</sub>S<sub>3</sub> from Volmer–Weber to Stranski–Krastanov, enabling the formation of large-grained Sb<sub>2</sub>S<sub>3</sub> onto the substrate during the hydrothermal deposition process. The adhesion work of Ce<sub>2</sub>S<sub>3</sub>/Sb<sub>2</sub>S<sub>3</sub> is 0.4616 J m<sup>-2</sup>, larger than that of 0.2112 J m<sup>-2</sup> for CdS/Sb<sub>2</sub>S<sub>3</sub>, which implies that the bond between Ce<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub> is stronger, resulting in the formation of a high-quality heterointerface with much more intimate contact.

Furthermore, the amorphous films will be transformed into compact and crystalline Sb<sub>2</sub>S<sub>3</sub> films after annealing at a high temperature of 370 °C in this work. The Sb<sub>2</sub>S<sub>3</sub> films would experience grain-coarsening during the postannealing treatment. According to the classical grain-coarsening mechanism, there is a thermodynamic driving force for favorable-oriented and/or large grains in a dense, polycrystalline thin film to increase in size. Note that the term “coarsening” here is used to imply a secondary grain-growth of an already-formed microstructure, as distinct from more general nuclei growth. Grain-coarsening often occurs in anisotropic films, where favorably-oriented grains involve rapid growth, giving rise to textured and large-grained films.<sup>[14a]</sup> In our case, all GBs in the Sb<sub>2</sub>S<sub>3</sub> films intersect the top surface and the bottom interface with the substrate. The favorably-oriented grains refer to the ones whose low-energy crystal planes include the top surface and the interface with the substrate. The system tends to maximize the area of those surfaces and interfaces via the growth

of the favorably oriented grains at the expense of the less favorably oriented grains. The coarsening rate of those favorably oriented grains can be expressed by Equation (1):<sup>[14a]</sup>

$$\frac{dr_s}{dt} = M \left[ \frac{(\gamma_s^* + \gamma_1^*) - (\gamma_s + \gamma_1) + \gamma_{GB}}{d} \right] \quad (1)$$

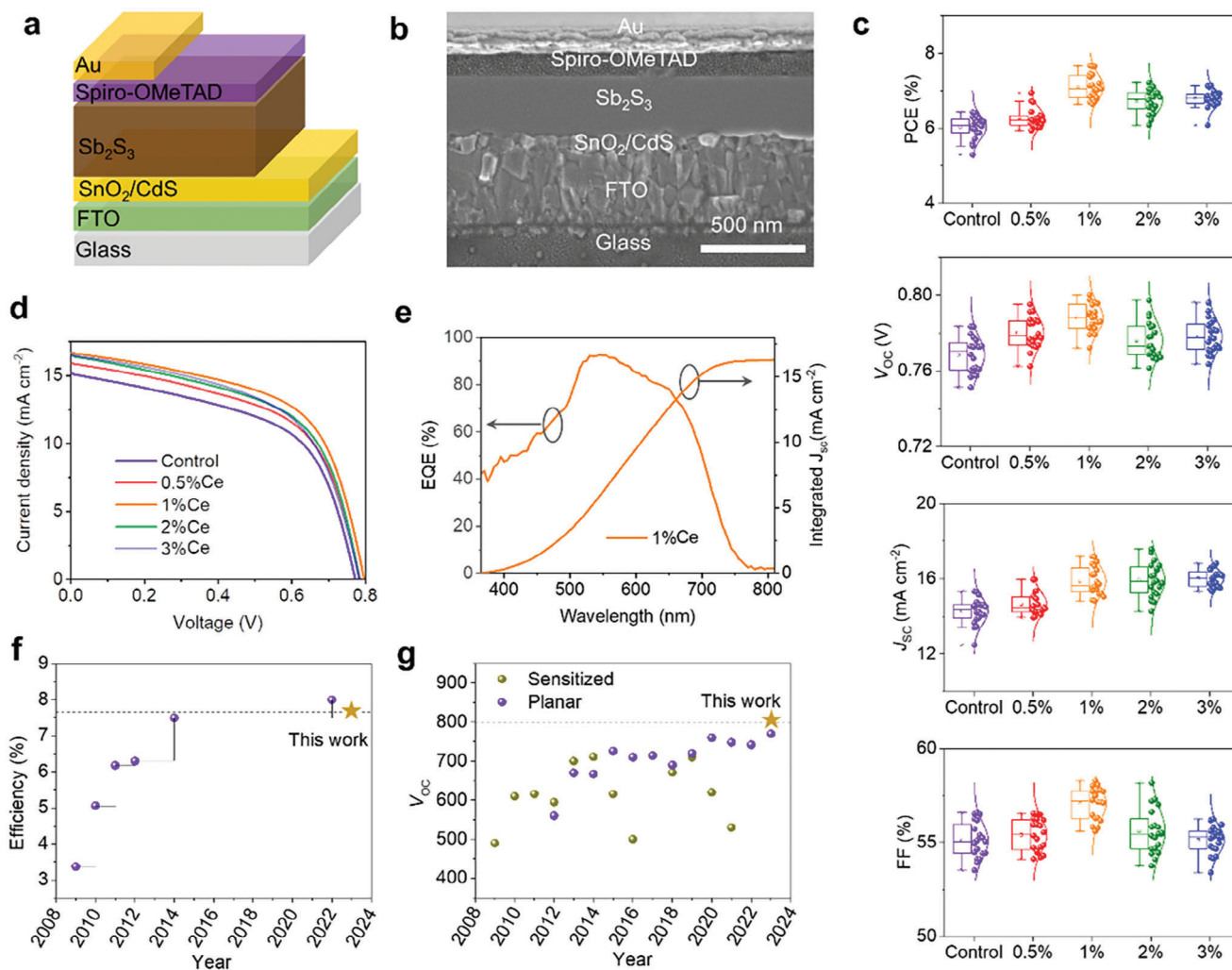
where  $r_s$  is the radius of the secondary grain,  $M$  is the GB mobility;  $\gamma_s^*$  and  $\gamma_1^*$  are the average energies of the top surface of the film and the interface with the substrate, respectively, of all the normal grains;  $\gamma_s$  and  $\gamma_1$  are the surface and interface energies, respectively, of the favorably oriented grains;  $\gamma_{GB}$  is the GB energy;  $d$  is the film thickness. Equation (1) implies that, by minimizing the energy ( $\gamma_1$ ) of the interface between the favorably oriented grains and the substrate through reasonable design of substrates for better adhesion, one can achieve rapid coarsening rate for grain-growth. Therefore, we suggest that the presence of Ce<sub>2</sub>S<sub>3</sub> interlayer contributes to the better adhesion between Sb<sub>2</sub>S<sub>3</sub> and the substrate, thus resulting in accelerated coarsening of favorably oriented Sb<sub>2</sub>S<sub>3</sub> grains. The likely scenario for the evolution at the growth stage of conventional Sb<sub>2</sub>S<sub>3</sub> films and Ce<sub>2</sub>S<sub>3</sub>-mediated Sb<sub>2</sub>S<sub>3</sub> films is illustrated schematically in Figure 4c.

Based on these discussions, it is concluded that the significantly increased Sb<sub>2</sub>S<sub>3</sub> grain sizes can be attributed to the Ce<sub>2</sub>S<sub>3</sub> interlayer influencing the nucleation and growth of Sb<sub>2</sub>S<sub>3</sub> deposited on top. The presence of the Ce<sub>2</sub>S<sub>3</sub> interlayer could result in improved heterojunction quality with more intimate binding between the Sb<sub>2</sub>S<sub>3</sub> layer and the substrate.

### 2.3. Device Performance of Sb<sub>2</sub>S<sub>3</sub> Planar Solar Cells

Figure 5a schematically illustrates the typical planar superstrate device configuration (n-i-p) of FTO/SnO<sub>2</sub>/CdS/Sb<sub>2</sub>S<sub>3</sub>/Spiro-OMeTAD/Au, in which Sb<sub>2</sub>S<sub>3</sub> is the absorber while SnO<sub>2</sub>/CdS and Spiro-OMeTAD serve as the electron and hole transport layers, respectively. From the cross-sectional SEM images of the full device stack (Figure 5b), the Sb<sub>2</sub>S<sub>3</sub> absorber layer is compact and uniform, with a thickness of 280 ± 10 nm. The photovoltaic parameters of such solar cells, each based on 20 devices, including  $V_{OC}$ ,  $J_{SC}$ , FF, and PCE, obtained under AM 1.5G illumination (100 mW cm<sup>-2</sup>), are given in the box charts of Figure 5c. The corresponding device photovoltaic parameters are summarized in Table 1. As shown, these devices exhibit good reproducibility and performance. With the addition of Ce<sup>3+</sup> into the precursor solution, the PCE of Sb<sub>2</sub>S<sub>3</sub> solar cells increased at first, before decreasing with further increases in Ce<sup>3+</sup> concentration. The control Sb<sub>2</sub>S<sub>3</sub> solar cells have an average PCE of 6.02%, whereas the average PCE was increased to 7.10% for the 1%Ce-Sb<sub>2</sub>S<sub>3</sub> device. The current density-voltage ( $J$ - $V$ ) curves of the champion control Sb<sub>2</sub>S<sub>3</sub> and Ce-Sb<sub>2</sub>S<sub>3</sub> solar cells, are shown in Figure 5d. The control Sb<sub>2</sub>S<sub>3</sub> solar cell has a  $V_{OC}$  of 772 mV,  $J_{SC}$  of 15.13 mA cm<sup>-2</sup>, FF of 54.94%, and PCE of 6.42%. The best-performing 1%Ce-Sb<sub>2</sub>S<sub>3</sub> device exhibits a PCE of 7.66%, coupled with a  $V_{OC}$  of 796 mV,  $J_{SC}$  of 16.67 mA cm<sup>-2</sup>, and FF of 57.72%. That is, the addition of 1%Ce<sup>3+</sup> leads to a relative PCE enhancement of 20% compared to the control device (or 1.24% absolute PCE increase). Figure 5f shows the evolution of the record PCE of Sb<sub>2</sub>S<sub>3</sub> solar cells over the past few years, which reflects that this work demonstrates a competitive device efficiency at a comparable level to the





**Figure 5.** a) Illustration and b) cross-sectional scanning electron microscopy (SEM) image of the device structure, which have the configuration: FTO/SnO<sub>2</sub>/CdS/Sb<sub>2</sub>S<sub>3</sub>/Spiro-OMeTAD/Au. c) The statistics of the performance parameters of the control Sb<sub>2</sub>S<sub>3</sub> device and Ce-Sb<sub>2</sub>S<sub>3</sub> devices obtained with the addition of different concentrations of Ce<sup>3+</sup> to the precursor solution. A total of 20 devices were measured for each condition, and the performance metrics of each device is shown as individual data points. d) J–V curves of the control Sb<sub>2</sub>S<sub>3</sub> and Ce-Sb<sub>2</sub>S<sub>3</sub> solar cells, measured under AM 1.5G (100 mW cm<sup>-2</sup>) illumination. e) External quantum efficiency (EQE) curves of best-performing 1%Ce-Sb<sub>2</sub>S<sub>3</sub> solar cells. f) Evolution in the record efficiency of Sb<sub>2</sub>S<sub>3</sub> solar cells. g) V<sub>OC</sub> values of previous work on well-developed planar and sensitized Sb<sub>2</sub>S<sub>3</sub> solar cells.

**Table 1.** Average photovoltaic performance parameters of the control and Ce-Sb<sub>2</sub>S<sub>3</sub> solar cells, measured under AM 1.5G illumination conditions.

Devices	V <sub>OC</sub> [mV]	J <sub>SC</sub> [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
Control	768 ± 9 (783)	14.26 ± 0.71 (15.33)	55.11 ± 0.93 (56.58)	6.02 ± 0.30 (6.42)
0.5%Ce	780 ± 8 (787)	14.67 ± 0.63 (15.97)	55.40 ± 0.85 (56.55)	6.27 ± 0.26 (6.94)
1%Ce	788 ± 7 (796)	15.91 ± 0.78 (17.19)	57.06 ± 0.84 (58.28)	7.10 ± 0.33 (7.66)
2%Ce	776 ± 10 (797)	15.99 ± 0.88 (17.57)	55.59 ± 1.17 (58.16)	6.72 ± 0.31 (7.21)
3%Ce	778 ± 9 (796)	15.99 ± 0.46 (16.82)	55.13 ± 0.74 (56.23)	6.79 ± 0.24 (7.13)

Format: mean ± standard deviation (best value).

recently-reported record efficiency of 8.00% for  $\text{Sb}_2\text{S}_3$  solar cells. Figure 5e presents the external quantum efficiency (EQE) spectrum of the best-performing 1%Ce- $\text{Sb}_2\text{S}_3$  solar cells. The device shows a broad light response, ranging from 350 to 750 nm, with the peak EQE exceeding 85% in the visible wavelength range. The integrated  $J_{\text{SC}}$  from the EQE spectrum is  $16.30 \text{ mA cm}^{-2}$ , consistent with the  $J_{\text{SC}}$  measured from the  $J$ - $V$  curve (within 5% deviation). The EQE spectra of the other devices are given in Figure S11 (Supporting Information). As shown, the  $J_{\text{SC}}$  enhancement for Ce- $\text{Sb}_2\text{S}_3$  solar cells mainly comes from the long-wavelength range of 510–710 nm, indicating that the Ce- $\text{Sb}_2\text{S}_3$  devices afford more efficient charge transport and collection. Considering that the control  $\text{Sb}_2\text{S}_3$  and Ce- $\text{Sb}_2\text{S}_3$  films have the same thicknesses, the enhancement in efficiency is attributed to more effective transport of charge-carriers in Ce- $\text{Sb}_2\text{S}_3$  than a higher density of charge-carriers being generated. Moreover, the Ce- $\text{Sb}_2\text{S}_3$  solar cells deliver improvements also in  $V_{\text{OC}}$  and FF. In particular, to the best of our knowledge, the  $V_{\text{OC}}$  obtained close to 800 mV is the highest value reported thus far for  $\text{Sb}_2\text{S}_3$  solar cells. Figure 5g gives the  $V_{\text{OC}}$  values of well-developed planar and sensitized  $\text{Sb}_2\text{S}_3$  solar cells (detailed in Table S6, Supporting Information). As shown, the trend in  $V_{\text{OC}}$  over the course of the development of  $\text{Sb}_2\text{S}_3$  photovoltaics has recently stagnated at around 550–750 mV. This work therefore sets a new record of  $V_{\text{OC}}$  for  $\text{Sb}_2\text{S}_3$  solar cells.

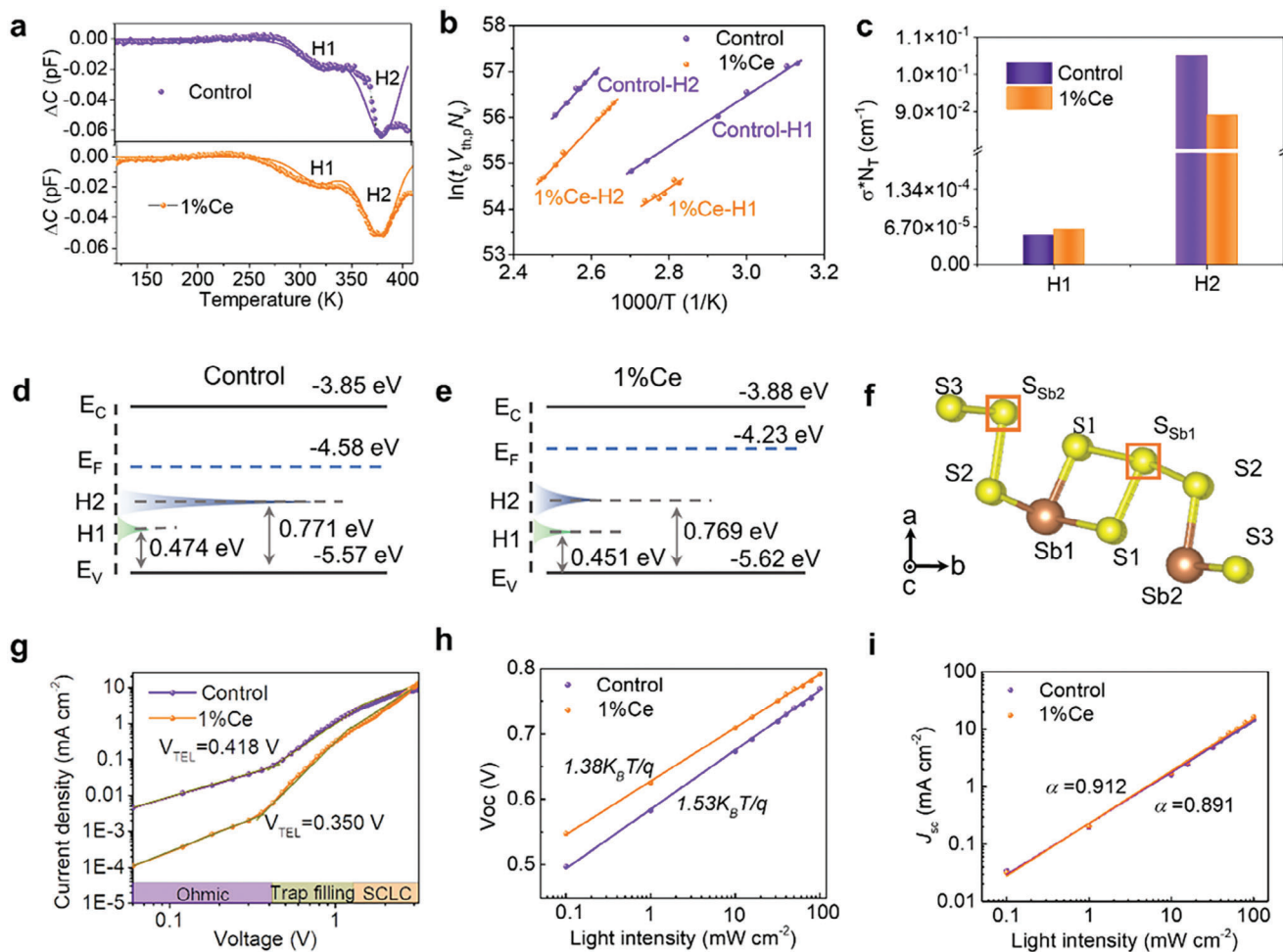
In addition to these improvements in the initial device efficiency, we found that Ce- $\text{Sb}_2\text{S}_3$  photovoltaics exhibited improved stability as well. We stored unencapsulated control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  devices in a cabinet with 15% relative humidity, and monitored the performance over time (Figure S12a, Supporting Information). The 1%Ce- $\text{Sb}_2\text{S}_3$  solar cell retained 97.1% of its initial efficiency after 30 days of storage, more stable in contrast to the control device that had 93.2% of the initial efficiency. Moreover, the unencapsulated devices also showed good stability under harsher damp-heat conditions (60% relative humidity, 50 °C). The control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  solar cells could retain 94.6% and 96.7% of their initial efficiencies, respectively, after 1-week of storage under these conditions (Figure S12b, Supporting Information).

It is worth noting that, increasing the  $\text{Ce}^{3+}$  concentration up to 5% and beyond resulted a sharp reduction in PCE (Figure S13a, Supporting Information). This phenomenon might be explained by the evolution in the morphology of  $\text{Sb}_2\text{S}_3$  films. The  $\text{Sb}_2\text{S}_3$  films appear to crack and peel off from the substrates, as reflected by SEM images of 5%Ce- $\text{Sb}_2\text{S}_3$  and 10%Ce- $\text{Sb}_2\text{S}_3$  films (Figure S13b,c, Supporting Information). This might have been caused by increased stress during the high-temperature annealing stage, causing cracking, delamination, and high roughness, similar to that reported for perovskite films.<sup>[28]</sup> Moreover, when  $\text{Ce}(\text{NO}_3)_3$  and  $\text{CeCl}_3$  were used to replace  $\text{Ce}(\text{CH}_3\text{COO})_3$  as the  $\text{Ce}^{3+}$  sources incorporated into the precursor solutions, the corresponding solar cells also delivered significantly enhanced performance (Figure S14, Supporting Information).

## 2.4. Defect Physics and Charge-Carrier Transport Properties

It is important to elucidate the defect characteristics of  $\text{Sb}_2\text{S}_3$  films and further establish the relationship between defects and

device performance. Deep-level transient spectroscopy (DLTS) was performed to explore the depth and quantity of defects in  $\text{Sb}_2\text{S}_3$  films. As shown in Figure 6a, both the control  $\text{Sb}_2\text{S}_3$  device and 1%Ce- $\text{Sb}_2\text{S}_3$  device present two negative DLTS signal peaks in the high temperature region due to the effect of multiple minority-carrier traps, i.e., hole defects in n-type  $\text{Sb}_2\text{S}_3$  films.<sup>[1c]</sup> Each DLTS signal was fitted by using deep-level transient Fourier spectroscopy (DLTFS) and decomposed into two hole defects of different depths denoted as H1 and H2. The defect characteristics, including activation energy ( $E_a$ ) and capture cross section ( $\sigma$ ), and trap concentration ( $N_T$ ) can be extracted from the linear fittings of the Arrhenius plots as given in Figure 6b, and the results are summarized in Table 2. The corresponding theory is given in Note S3 (Supporting Information). The  $E_a$  values of H1 and H2 are 0.45 and 0.77 eV, respectively. It is known that  $\text{Sb}_2\text{S}_3$  consists of  $[\text{Sb}_4\text{S}_6]_n$  chains which have five nonequivalent atomic sites, i.e., Sb1, Sb2, S1, S2, and S3. The quasi-1D crystal structure involves the presence of multiple defects in  $\text{Sb}_2\text{S}_3$ , including five vacancies ( $V_{\text{Sb1}}$ ,  $V_{\text{Sb2}}$ ,  $V_{\text{S1}}$ ,  $V_{\text{S2}}$ , and  $V_{\text{S3}}$ ), five anti-sites ( $S_{\text{Sb1}}$ ,  $S_{\text{Sb2}}$ ,  $S_{\text{S1}}$ ,  $S_{\text{S2}}$ , and  $S_{\text{S3}}$ ), and two interstitials ( $\text{Sb}_i$  and  $\text{S}_i$ ), as predicted by previous theoretical calculations.<sup>[7a,b]</sup> By comparing the depth of defects obtained from measurements with the transition levels obtained from calculations, the H1 and H2 traps are consistent with two anti-site defects,  $S_{\text{Sb1}}$  and  $S_{\text{Sb2}}$ . It is revealed that both devices share identical types of deep-level defects; however, the concentrations of the H1 and H2 defects differ. Moreover, our hydrothermally deposited  $\text{Sb}_2\text{S}_3$  films exhibit much lower defect density than  $\text{Sb}_2\text{S}_3$  prepared by thermal evaporation.<sup>[29]</sup> The trapping capability of defects can be quantified by using the thermal trapping rate ( $C_{\text{trap}}$ ), which is expressed by the equation  $C_{\text{trap}} = 1/\tau_{\text{trap}} = \nu\sigma N_T$ , where  $\tau_{\text{trap}}$  is the carrier lifetime associated with the trap-assisted Shockley–Read–Hall (SRH) recombination and  $\nu$  is the thermal velocity of charge related to the intrinsic charge transport feature of semiconductors. Therefore, minimizing defect density, particularly those with large capture cross sections, would increase minority carrier lifetimes and hence enhance  $V_{\text{OC}}$ . Here the impact of deep-level defects on the trapping of carriers of the control  $\text{Sb}_2\text{S}_3$  device and 1%Ce- $\text{Sb}_2\text{S}_3$  device can be simply compared by the value of  $\sigma N_T$ , as given by the statistical histogram of calculated  $\sigma N_T$  for different hole traps (Figure 6c). It is revealed that H2 dominates charge trapping in absorber films in view of its larger  $\sigma N_T$  value and greater energy depth. In contrast, the H1 defect would have limited carrier trapping capability because of its low capture cross section on the order of  $10^{-18} \text{ cm}^2$ , three orders of magnitude lower the  $10^{-15} \text{ cm}^2$  value for the H2 defect. Hence, we assign H2 as the trap that is mainly responsible for the  $V_{\text{OC}}$  loss in the space charge region (SCR) of the solar cells. Compared to the control  $\text{Sb}_2\text{S}_3$  device, the  $\sigma N_T$  for the H2 defect in 1%Ce- $\text{Sb}_2\text{S}_3$  is decreased owing to a reduction in defect density. The band edge position and defect levels are illustrated in Figure 6d,e. Figure 6f gives the illustration of the defects of  $S_{\text{Sb1}}$  and  $S_{\text{Sb2}}$  in a  $[\text{Sb}_4\text{S}_6]_n$  unit of  $\text{Sb}_2\text{S}_3$  crystal structure. Since the depth of defects reflects the difficulty of charge emission from the traps, the H1 and H2 defects located at more than 0.3 eV above the VB would trap carriers without re-emission, thus acting as recombination centers and resulting in reductions in  $V_{\text{OC}}$ . These results suggest that the Ce- $\text{Sb}_2\text{S}_3$  films could decrease the defect density in absorber films and suppress charge-carrier recombination in solar cells.



**Figure 6.** a) Deep-level transient spectroscopy (DLTS) signals from the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  devices. b) Arrhenius plots derived from DLTS signals. The data points were obtained by calculating internal transients included in DLTS signals with the discrete Laplace transform, and the solid lines are corresponding linear fits. H1 and H2 correspond to  $\text{S}_{\text{Sb}1}$  and  $\text{S}_{\text{Sb}2}$  anti-site defects, respectively. c) The statistical histogram of calculated  $\sigma N_T$  for different hole traps in the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  devices. d,e) Schematic of band edge positions and defect levels of the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$ , respectively, including CB ( $E_C$ ) and VB ( $E_V$ ) edges, Fermi level ( $E_F$ ), and defect energy levels (H1, H2), relative to the vacuum level. f) Illustration of  $\text{S}_{\text{Sb}1}$  and  $\text{S}_{\text{Sb}2}$  defects in a  $[\text{Sb}_4\text{S}_6]_n$  unit of  $\text{Sb}_2\text{S}_3$  crystal structure. g) Space-charge limit current density (SCLC) measurements of the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  based on the electron-only structure device of FTO/CdS/ $\text{Sb}_2\text{S}_3$ /PCBM/Au. h,i) The dependence of  $V_{\text{OC}}$  and  $J_{\text{SC}}$  on the light intensity for the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  solar cells.

An increase in the band-tail states extending into the bandgap corresponds to an increase in the Urbach energy ( $E_U$ ), which is a characteristic measure of the level of disorder.<sup>[30]</sup> As shown in the absorption spectra (Figure S15a, Supporting Information), the addition of  $\text{Ce}^{3+}$  decreases the band tailing of  $\text{Sb}_2\text{S}_3$  films.

The bandgaps of control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  films were estimated to be 1.73 and 1.74 eV by using Tauc plots given in Figure S15b (Supporting Information). We used photothermal deflection spectroscopy (PDS), which is a highly sensitive technique to measure weak absorption at or below the bandgap, to

**Table 2.** Defect characteristics including the trap energy level ( $E_T$ ), cross-section ( $\sigma$ ), and trap concentration ( $N_T$ ) in the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  devices.

Devices	Trap	$E_T$ [eV]	$\sigma$ [ $\text{cm}^2$ ]	$N_T$ [ $\text{cm}^{-3}$ ]	$\sigma N_T$ [ $\text{cm}^{-1}$ ]
control $\text{Sb}_2\text{S}_3$	H1	$E_V + 0.474$	$3.94 \times 10^{-18}$	$1.33 \times 10^{13}$	$5.24 \times 10^{-5}$
	H2	$E_V + 0.771$	$2.32 \times 10^{-15}$	$4.52 \times 10^{13}$	$1.05 \times 10^{-1}$
1%Ce- $\text{Sb}_2\text{S}_3$	H1	$E_V + 0.451$	$5.17 \times 10^{-18}$	$1.22 \times 10^{13}$	$6.30 \times 10^{-5}$
	H2	$E_V + 0.769$	$6.85 \times 10^{-15}$	$1.30 \times 10^{13}$	$8.90 \times 10^{-2}$

evaluate  $E_U$ . The Urbach energies of  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  film samples were fitted to be 176 and 169 meV, respectively (Figure S15c,d, Supporting information). Although the obtained absolute  $E_U$  values might be overestimated due to the influence of the FTO/CdS substrate on the infrared absorption, which requires further study, the slight decrease in Urbach energy for 1%Ce- $\text{Sb}_2\text{S}_3$  is consistent in a decrease in sub-bandgap state density.

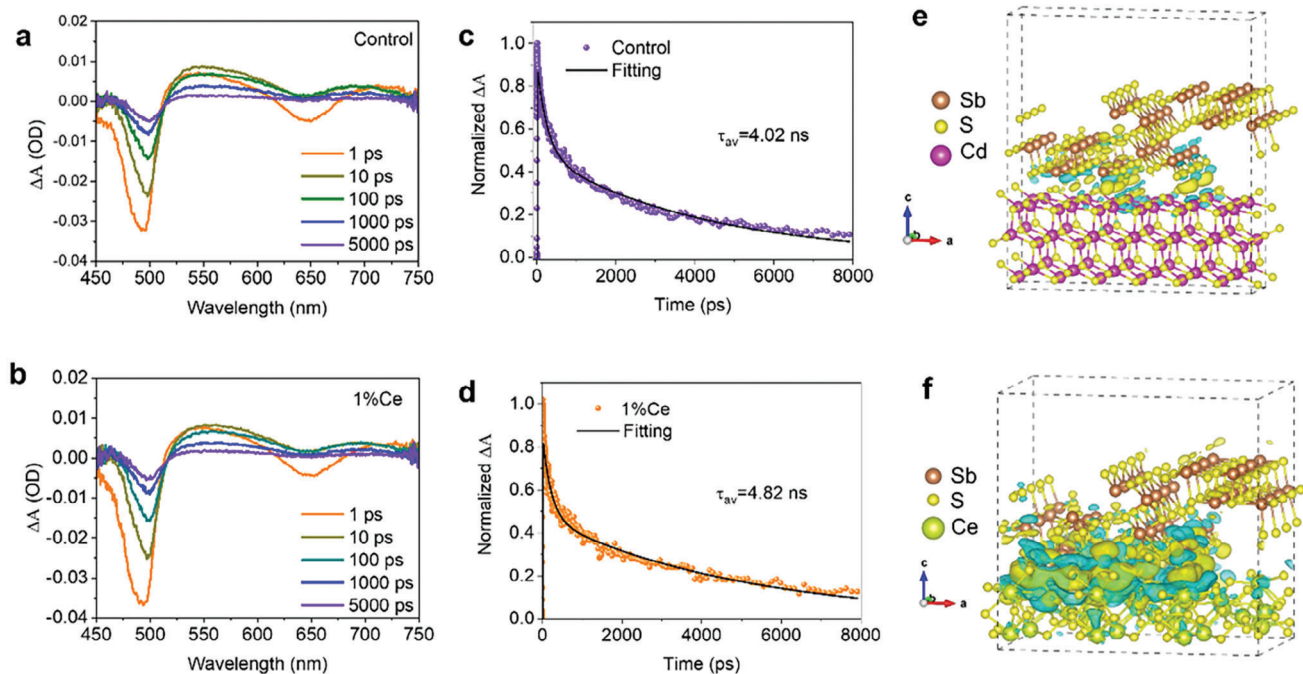
Space charge limited current (SCLC) measurements were conducted to evaluate the overall trap-state density of absorber films based on the electron-only devices FTO/CdS/ $\text{Sb}_2\text{S}_3$ /PCBM/Au. As shown in Figure 6g, at low bias voltage, the linear  $I$ - $V$  curve suggests a typical Ohmic response. As the bias voltage increases and reaches the trap-filled limiting voltage ( $V_{\text{TFL}}$ ), the curve presents a nonlinear feature because of the filling of injected carriers into trap-states.<sup>[23]</sup> The trap-state density can be estimated by using the equation  $V_{\text{TFL}} = qn_t L^2 / 2\epsilon_r \epsilon_0$ , where  $n_t$  is the trap-state density,  $q$  is the elementary charge ( $1.60 \times 10^{-19}$  C),  $\epsilon_0$  is the vacuum permittivity ( $8.85 \times 10^{-12}$  F m<sup>-1</sup>),  $\epsilon_r$  is the relative permittivity of  $\text{Sb}_2\text{S}_3$  (6.67), and  $L$  is the thickness of  $\text{Sb}_2\text{S}_3$  film ( $\approx 280$  nm). The  $V_{\text{TFL}}$  values of the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  devices are estimated to be 0.418 and 0.350 V, respectively. Hence the 1%Ce- $\text{Sb}_2\text{S}_3$  device involves reduced trap-state density ( $3.29 \times 10^{15}$  cm<sup>-3</sup>) compared to the control  $\text{Sb}_2\text{S}_3$  device ( $3.94 \times 10^{15}$  cm<sup>-3</sup>). This reduction in the trap-state density is consistent with the result from DLTS characterization. The difference in the carrier concentrations obtained from DLTS and SCLC might be due to the fact that these two measurements were performed under different conditions. Firstly,  $I$ - $V$  measurements from SCLC are steady state measurements, whereas DLTS involves transient measurements.<sup>[31]</sup> Secondly, the SCLC measurement is performed at room temperature to observe the total trap density, while the DLTS measurement was conducted from 120 to 410 K in this work. Thirdly, the sensitivity of SCLC and DLTS toward defects of different types and depths are also different. These factors may explain the different trap state densities derived from both techniques.

Light intensity-dependent  $J$ - $V$  measurement is an effective strategy for assessing trap-assisted charge recombination loss mechanisms in solar cells. The dependences of  $V_{\text{OC}}$  and  $J_{\text{SC}}$  on the light intensity were conducted for the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  solar cells. The corresponding semi-logarithmic plots, as shown in Figure 6h,i, can be achieved according to the relationship between  $V_{\text{OC}}$  (or  $J_{\text{SC}}$ ) and light intensity as described by the relations  $V_{\text{OC}} \propto (nK_B T/q) \ln(I)$  and  $J_{\text{SC}} \propto I^\alpha$ ,<sup>[32]</sup> where  $I$  is the light intensity,  $K_B$  is the Boltzmann constant,  $T$  represents the absolute temperature,  $q$  is the elementary charge, and the values of  $n$  and  $\alpha$  reflect the level of charge recombination. A diode ideality factor of unity occurs when recombination is entirely radiative, and a larger value implies more severe defect-assisted SRH recombination.<sup>[44]</sup> The 1%Ce- $\text{Sb}_2\text{S}_3$  device delivers a smaller  $n$  of 1.38 than the control  $\text{Sb}_2\text{S}_3$  device ( $n = 1.53$ ), which is consistent with a reduction in nonradiative recombination. Moreover, as a result of the space charge effect, the value of  $\alpha$  is often smaller than 1. Compared to the  $\alpha$  value of 0.891 for the control device, the 1%Ce- $\text{Sb}_2\text{S}_3$  solar cell has a slightly larger  $\alpha$  value of 0.912. However, these changes in  $\alpha$  are too small to interpret. We further performed electrochemical impedance spectroscopy to investigate the charge transfer and recombination dynamics in solar cells.

Figure S16 (Supporting Information) shows the Nyquist plots of impedance spectra measured under dark, and corresponding fitting results based on the equivalent circuit model given in the inset are summarized in Table S7 (Supporting Information).<sup>[33]</sup> Clearly, the 1%Ce- $\text{Sb}_2\text{S}_3$  device shows an increased recombination resistance at the CdS/ $\text{Sb}_2\text{S}_3$  interface ( $R_{\text{rec}} = 16.80$  k $\Omega$  cm<sup>-2</sup>) in contrast to the control device ( $R_{\text{rec}} = 7.83$  k $\Omega$  cm<sup>-2</sup>). A large recombination resistance would result in suppressed charge recombination and improved charge collection in photovoltaic devices.

We also carefully analyzed  $J$ - $V$  curves of the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  solar cells measured in the dark (Figure S17, Supporting Information), from which the parameters of junction ideality factor ( $A$ ), the reverse saturation current density ( $J_0$ ), the series resistance ( $R_s$ ), and the shunt conductance ( $G$ , i.e.,  $1/R_{\text{sh}}$ ) can be extracted.<sup>[2a]</sup> The detailed description is provided in Note S4 (Supporting Information), and the overall fitting parameters are summarized in Table S8 (Supporting Information). The ideality factor plays a critical role to evaluate the junction quality as it reveals the main recombination mechanism of a p-n heterojunction. The calculated ideality factor of 1%Ce- $\text{Sb}_2\text{S}_3$  device ( $A = 1.67$ ) is smaller than that of the control  $\text{Sb}_2\text{S}_3$  device ( $A = 2.07$ ), implying the effective suppression of charge-carrier recombination for the 1%Ce- $\text{Sb}_2\text{S}_3$  device. Moreover, the 1%Ce- $\text{Sb}_2\text{S}_3$  device obtains the lower  $J_0$  ( $8.7 \times 10^{-8}$  mA cm<sup>-2</sup>), the smaller  $R_s$  ( $4.93$   $\Omega$  cm<sup>-2</sup>), and the smaller  $G$  ( $0.005$  mS cm<sup>-2</sup>) compared to the control  $\text{Sb}_2\text{S}_3$  device ( $J_0 = 1.5 \times 10^{-6}$  mA cm<sup>-2</sup>,  $R_s = 13.42$   $\Omega$  cm<sup>-2</sup>,  $G = 0.023$  mS cm<sup>-2</sup>), indicating the enhancement in charge extraction capability. These results demonstrated the improved heterojunction quality for 1%Ce- $\text{Sb}_2\text{S}_3$  devices as a result of reduced shunt-current leakage, contributing to the improvement of device performance.<sup>[19]</sup>

Ultrafast transient absorption (TA) spectroscopy measurements were performed on the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  films deposited onto FTO/SnO<sub>2</sub>/CdS substrates without any hole extraction layer for this study to understand the charge-carrier kinetics further. As shown in Figure 7a,b, the TA spectra show pronounced ground state bleach (GSB) negative peaks and positive photoinduced absorption (PIA) peaks. Specifically, the GSB peaks at 460–510 and 610–680 nm can be assigned to the state filling of CdS films and the ground state absorption of  $\text{Sb}_2\text{S}_3$  films, respectively; the typical PIA peak appearing at 520–620 nm can be attributed to the formation of sulfide radical ( $\text{S}^-$ ) due to photoexcited holes localized on the S atom of  $\text{Sb}_2\text{S}_3$  lattice.<sup>[1c,4a,29,34]</sup> The transient dynamics are retrieved from the pseudocolor pictures (Figure S18a,b, Supporting Information). The transient kinetic decay (scatter) monitored at 560 nm for the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  films are given in Figure 7c,d, which are well fitted by a phenomenological biexponential equation (Note S5, Supporting Information), and the corresponding results are listed in Table S9 (Supporting Information).<sup>[2b]</sup> The PIA peak gradually decreases as a result of the decay of trapped holes, i.e., the  $\text{S}^-$  species, which we here attribute to nonradiative carrier recombination in  $\text{Sb}_2\text{S}_3$  films.<sup>[4a,35]</sup> As shown, the 1%Ce- $\text{Sb}_2\text{S}_3$  sample exhibits larger  $\tau_{\text{av}}$  values (4.82 ns) that of the control  $\text{Sb}_2\text{S}_3$  sample (4.02 ns). The prolonged lifetime in the 1%Ce- $\text{Sb}_2\text{S}_3$  sample suggests the suppression of the bulk and/or interfacial charge-carrier recombination, consistent with the results from DLTS characterizations. That is, the TA analysis reveals a slower charge



**Figure 7.** a,b) Transient absorption (TA) spectra obtained at 1, 10, 100, 1000, and 5000 ps pump-probe delay for control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  film samples. Excitation was with a 400 nm wavelength pulsed laser at a fluence of  $251 \mu\text{J cm}^{-2} \text{pulse}^{-1}$  and a repetition rate of 1000 Hz. c,d) Transient kinetic decay (scatter) and corresponding biexponential curve fittings (solid line) monitored at 560 nm of the control  $\text{Sb}_2\text{S}_3$  and 1%Ce- $\text{Sb}_2\text{S}_3$  films.  $\Delta A$  is defined as the change in the absorption of the sample before and after pumping. e,f) Diagram of the charge density difference analysis of the heterointerfaces of  $\text{CdS}/\text{Sb}_2\text{S}_3$  and  $\text{Ce}_2\text{S}_3/\text{Sb}_2\text{S}_3$ .

recombination rate in 1%Ce- $\text{Sb}_2\text{S}_3$  films with larger grains. The prolonged lifetime of photoexcited minority hole carriers would eventually result in the improvement of  $V_{\text{OC}}$ .

Furthermore, we carried out charge density difference analysis to investigate the interaction at the heterointerfaces of  $\text{CdS}/\text{Sb}_2\text{S}_3$  and  $\text{Ce}_2\text{S}_3/\text{Sb}_2\text{S}_3$ . As shown in Figure 7e,f, the yellow area means that there is charge accumulation there, while the blue area means that there is charge loss there. Due to the value of the isosurfaces in two models being identical, it is shown that, compared to the case of  $\text{CdS}/\text{Sb}_2\text{S}_3$ , the  $\text{Ce}_2\text{S}_3$  surface has stronger charge transfer with the  $\text{Sb}_2\text{S}_3$  surface. This calculation result corroborates the previous view that the bonding at  $\text{Ce}_2\text{S}_3/\text{Sb}_2\text{S}_3$  heterointerface is stronger than that of the  $\text{CdS}/\text{Sb}_2\text{S}_3$  heterointerface. That is, the presence of  $\text{Ce}_2\text{S}_3$  contributes to the formation of a more ideal heterointerface, which would afford improved charge-carrier transport properties at the heterojunction in  $\text{Sb}_2\text{S}_3$  solar cells.

### 3. Conclusion

In this work, we demonstrate a facile grain engineering strategy to deposit large-grained  $\text{Sb}_2\text{S}_3$  films by adding  $\text{Ce}^{3+}$  into the precursor solution for hydrothermal deposition. Careful experimental characterization and first-principles calculations reveal that the incorporation of  $\text{Ce}^{3+}$  results in the generation of an ultrathin  $\text{Ce}_2\text{S}_3$  interlayer at the  $\text{CdS}/\text{Sb}_2\text{S}_3$  interface, which we propose promotes heterogeneous nucleation and horizontal growth of  $\text{Sb}_2\text{S}_3$  grains due to a reduced free energy barrier for nucleation, as well as lower interfacial energy. The champion  $\text{Sb}_2\text{S}_3$  solar

cell delivers a considerable PCE of 7.66%, superior to the control (6.42% PCE). High  $V_{\text{OC}}$ 's result, reaching values close to 800 mV, and is, to our knowledge at the time of publication, the new record for  $\text{Sb}_2\text{S}_3$  solar cells. This enhanced performance might be attributed not only to suppressed charge-carrier recombination because of reduced detrimental defects at GBs and/or the  $\text{CdS}/\text{Sb}_2\text{S}_3$  heterointerface, but also to improved charge-carrier transport across the heterojunction in  $\text{Sb}_2\text{S}_3$  solar cells. Furthermore, although the large  $V_{\text{OC}}$  loss remains a bottleneck for the performance improvement of  $\text{Sb}_2\text{S}_3$  solar cells, this work provides an important strategy that can be more broadly applied to increase the grain size and reduce the  $V_{\text{OC}}$  loss more generally in polycrystalline solar cells.

### 4. Experimental Section

**Device Fabrication:** Firstly, we fabricated  $\text{SnO}_2/\text{CdS}$  electron transport layers on fluorine-doped tin oxide (FTO,  $\approx 15 \Omega \text{sq}^{-1}$ ) conductive glass substrates, which were thoroughly cleaned in advance by using detergent, deionized (DI) water, acetone, ethanol, and isopropanol, each for 20 min with ultrasonication and in sequence, followed by drying with nitrogen ( $\text{N}_2$ ) airflow. The ultrathin  $\text{SnO}_2$  layer was deposited by spin-coating commercial  $\text{SnO}_2$  colloidal dispersion (15% in  $\text{H}_2\text{O}$ , Alfa Aesar) that was diluted seven times with DI water onto the conductive substrate at a speed of 3000 rpm for 30 s. Then as-prepared  $\text{SnO}_2$  films were further annealed at  $150^\circ\text{C}$  for 30 min. We used the CBD method to deposit  $\text{CdS}$  buffer layers. Typically, 30 mL of  $15 \times 10^{-3} \text{ M Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (99%, Macklin) and 39 mL of ammonia solution in water (25%–28%, Sinopharm) were mixed together and stirred for 2 min. Then, 19.2 mL of 1.2 M thiourea (99.0%, Sinopharm) and 210 mL of DI water were further

added, followed by another 2 min stirring. FTO/SnO<sub>2</sub> substrates were vertically immersed into such precursor solutions and maintained at 65 °C for 14 min with continuous stirring. Here, the thicknesses of SnO<sub>2</sub> and CdS layers in FTO/SnO<sub>2</sub>/CdS substrates were about 10 and 60 nm, respectively, according to our previous work.<sup>[32b]</sup> Afterwards, as-prepared CdS layers were treated with CdCl<sub>2</sub> by spin-coating 0.088 M CdCl<sub>2</sub>·2.5H<sub>2</sub>O (99.0%, Sinopharm) in methanol solution onto CdS layers, followed by further annealing in air at 400 °C for 10 min. Secondly, the Sb<sub>2</sub>S<sub>3</sub> absorber films were deposited onto FTO/SnO<sub>2</sub>/CdS substrates by hydrothermal deposition, in which C<sub>4</sub>H<sub>4</sub>KO<sub>7</sub>Sb·0.5H<sub>2</sub>O (99.0%, Sinopharm) and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O (99.5%, Aladdin) were employed as Sb and S sources, respectively. A mixture solution with 20 × 10<sup>-3</sup> M C<sub>4</sub>H<sub>4</sub>KO<sub>7</sub>Sb·0.5H<sub>2</sub>O and 80 × 10<sup>-3</sup> M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O diluted in 40 mL DI water was added into a 50 mL Teflon tank, and FTO/SnO<sub>2</sub>/CdS substrates were immersed into the mixture with the conducting side facing down inside the tank and tilted at an angle of ≈75° with respect to the horizontal plane. For the addition of lanthanide ions, particular lanthanide salts were used in this work. The type and the amount of salts were stated in corresponding parts of main text and supporting information. The Teflon tank was then sealed and kept at 135 °C for 180 min. When the reaction ended and the tank cooled down, the substrates were taken out, followed by rinsing with DI water and drying with N<sub>2</sub> flow. Then, as-deposited films were annealed at 370 °C for 10 min in a N<sub>2</sub> filled glovebox. Thirdly, the hole transport layer was deposited onto absorber films by spin-coating the precursor at a speed of 3000 rpm for 30 s, followed by annealing under 100 °C for 10 min on a hot plate. Here the hole transport layer precursor was prepared by mixing 36.6 mg spiro-OMeTAD (99.8%, Xi'an Polymer Light Technology Corp.), 14.5 μL tert-butylpyridine (TBP, 96%, Aladdin), and 9.5 μL 0.52 g mL<sup>-1</sup> of lithium bis(trifluoromethylsulfonyl)imide salt (99.95%, Aladdin) dissolved in acetonitrile (99%, Aladdin) in 1 mL chlorobenzene (anhydrous, 99.8%, Sigma). Finally, superstrate Sb<sub>2</sub>S<sub>3</sub> solar cells were completed by thermal evaporation of 80 nm Au as back electrodes.

**Characterization:** XRD characterization was performed on an X'Pert PRO MPD diffractometer with the Bragg Brentano geometry, and a Cu K<sub>α</sub> X-ray source (λ = 1.5406 Å) was used. SEM images of film samples were collected on a JEOL field emission scanning electron microscope (JSM-6700F) equipped with EDS. The GB densities were obtained by depicting the GB grooves in SEM images of films using Adobe Photoshop software. AFM images were collected on a Bruker atomic force microscope (Dimension Icon); SCM-PIT probes were used in both the KPFM and c-AFM measurements, and the scanning area was 5 × 5 μm. The lattice structure was studied by TEM (Talos F200S), and the specimens were made by using a FIB technique with a microsampling system (Thermo Scientific Helios 5 CX). The element distribution of thin films was obtained by using SIMS (TOF-SIMS 5, ION-TOF GmbH), in which the sputtering source is O<sub>2</sub><sup>+</sup> with the energy of 1 KeV and the area of 86 × 86 μm. Ultraviolet-visible absorption spectra were collected on a CARY 5000 Agilent spectrophotometer. The absorbance was obtained by using the equation  $A = -\log_{10}(T)$ , where  $A$  is the absorbance, and  $T$  is the transmittance. XPS was conducted on a Thermo Scientific K-Alpha spectrometer (Al K<sub>α</sub> excitation, 1486.6 eV). UPS was performed on Thermo ESCALAB XI (He I excitation, 21.22 eV).  $J$ - $V$  curves of solar cells were measured under the illumination of 1-sun (AM 1.5G, 100 mW cm<sup>-2</sup>) by using a Newport Oriol Sol 3A Solar Simulator, combined with a Keithley 2400 digital source meter. The active area of devices was defined by a 0.06 cm<sup>2</sup> mask. EQE measurements were conducted on a QTest Station 1000 ADI system (CrownTech, Inc) under the DC mode, and the excitation source was a 300 W xenon lamp (CT-XE-300) which was split into specific wavelengths via a M24-S 1/4m monochromator. Impedance spectra were collected on a Zahner workstation (Zennium Pro.) with an applied voltage of 0.6 V and a scanning range of 1 Hz to 1 MHz under dark, and the spectra were fitted by using Z-view software. The DLTS characterization was performed on a Phystech FT-1230 HERA DLTS system with a laser excitation at the wavelength of 405 nm and the power of 10 mW. The capacitances were recorded by a Boonton 7200 Phystech capacitance meter (high frequency, 1 MHz). The device samples were placed in the liquid helium cryostat with a temperature scan ranging from 120 to 410 K at an interval of 2 K. The reverse bias, optical pulse width, and period width were -0.4 V, 100 ms, and 200 ms, respec-

tively. PDS was performed in a custom setup working in the transverse configuration. A tunable light source consisting of a grating monochromator coupled with a quartz-tungsten halogen lamp served as a pump, after modulating with a mechanical chopper inducing periodic temperature oscillations at the sample surface. A probe laser beam was passed parallel to the sample plane, with its path deviated by the temperature gradient in the heat-transfer liquid (3 M Fluorinert FC-72) surrounding the sample. The beam deflection amplitude was measured with a quadrant photodiode and demodulated with a lock-in amplifier (Stanford Research Systems SR830). The ultrafast TA properties of films were performed on a Helios Ultrafast pump-probe system, where a nondegenerate pump-probe configuration was used to probe the transient dynamics in the femtosecond to nanosecond time region (50 fs to 7 ns) under ambient conditions. The pump pulses of 400 nm was obtained by using a beta barium borate (BBO) crystal to double the 800 nm pulse generated on an optical parametric amplifier, and the white light continuum probe pulses was formed by 800 nm femtosecond with a 2 mm sapphire plate for the 400–800 nm wavelength range.

**Calculations:** All first-principles calculations were performed via density functional theory (DFT) by means of generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE), implemented by the Vienna Ab Initio Simulation Package (VASP).<sup>[36]</sup> The projected augmented wave (PAW) pseudopotentials were adopted with a cutoff energy of 450 eV in the whole calculation process.<sup>[37]</sup> The convergence criterion for the electronic self-consistent field loop was set to be 10<sup>-5</sup> eV. The crystal structures, the surface structure, and the heterojunction structure were optimized until the residual force were below 0.03, 0.05, and 0.05 eV Å<sup>-1</sup>, respectively. The Sb<sub>2</sub>S<sub>3</sub> (120), CdS (100), and Ce<sub>2</sub>S<sub>3</sub> (001) surfaces were used to simulate the exposed surfaces. The CdS (100) and Sb<sub>2</sub>S<sub>3</sub> (120) surfaces were selected as exposed surfaces to form the CdS/Sb<sub>2</sub>S<sub>3</sub> heterojunction based on XRD patterns, while Ce<sub>2</sub>S<sub>3</sub> (001) was suggested to be the exposed surface to combine with Sb<sub>2</sub>S<sub>3</sub> (120) by carefully examining the HRTEM image at the interface of CdS/Sb<sub>2</sub>S<sub>3</sub>. Moreover, the Ce<sub>2</sub>S<sub>3</sub> (001) was a nonpolar surface similar to the exposed (100) surface of CdS, so that the quality of two heterojunctions could be compared more objectively. Furthermore, for the surface relaxation, a vacuum layer with a thickness of 15 Å was used and the bottom layers of atoms were bound to simulate the bulk phase. The Ce<sub>2</sub>S<sub>3</sub>/Sb<sub>2</sub>S<sub>3</sub> heterointerface was generated with 1 × 5 × 1 Sb<sub>2</sub>S<sub>3</sub> surface and 3 × 1 × 1 Ce<sub>2</sub>S<sub>3</sub> surface supercells, with a vertical spacing about 2.4 Å and lattice parameters of  $a = 24.025$  Å,  $b = 15.386$  Å,  $c = 23.000$  Å. The CdS/Sb<sub>2</sub>S<sub>3</sub> heterointerface was generated with 1 × 2 × 1 Sb<sub>2</sub>S<sub>3</sub> surface and 6 × 1 × 1 CdS surface supercells, with a vertical spacing about 2.4 Å and lattice parameters of  $a = 25.492$  Å,  $b = 7.281$  Å,  $c = 28.000$  Å. The D3 Grimme dispersion correction was employed during the calculation of heterointerface formation energies.<sup>[38]</sup> The corresponding k-point spacing of all models was less than 0.3 Å<sup>-1</sup>. Specifically, the Brillouin zone of Ce<sub>2</sub>S<sub>3</sub> surface, CdS surface, Sb<sub>2</sub>S<sub>3</sub> surface, Ce<sub>2</sub>S<sub>3</sub>/Sb<sub>2</sub>S<sub>3</sub> heterojunction, and CdS/Sb<sub>2</sub>S<sub>3</sub> heterojunction were sampled by (4 × 2 × 1), (6 × 4 × 1), (1 × 9 × 1), (1 × 2 × 1), and (1 × 3 × 1) k-points mesh with Gamma point centered, respectively. The calculating formula and detailed processes for formation energy, surface energy, interface adhesive work, interfacial energy, and charge density difference analysis can be found in Note S6 (Supporting Information).

**Statistical Analysis:** All statistical analyses were performed using Origin 2019 (OriginLab Corp). The data from SEM, AFM, TEM, SIMS, XPS, UPS, UV–Vis, PDS, contact angles,  $J$ - $V$ , EQE, EIS, and TA spectra shown in the paper are the original data without normalization. The data from XRD and TA kinetic decays were normalized to 1. The PCE data points of 1-week device stability tests were normalized to the PCEs measured before aging. Linear fittings were applied to UPS,  $V_{OC}$ , and  $J_{SC}$  versus light intensity, SCLC, and PDS plots. The data points of Arrhenius plots derived from DLTS signals were achieved by calculating internal transients included in DLTS signals with the discrete Laplace transform, and further processed with a linear fitting. Biexponential decay function was applied to TA kinetic decays to analyze the carrier dynamics. Quantitative data were expressed as the mean ± standard deviation. The statistical distribution for the PCE,  $V_{OC}$ ,  $J_{SC}$ , and FF were obtained from 20 devices, and the lower whisker, lower box edge, middle line, upper box edge, and upper whisker

refer to minimum, 25th percentile, median, 75th percentile, and maximum of the dataset, respectively.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the Oxford University Research Archive, with the DOI: 10.5287/ora-gjqokbbde . <http://dx.doi.org/10.5287/ora-gjqokbbde>

## Keywords

defects, grain engineering, nucleation and growth, open-circuit voltage, Sb<sub>2</sub>S<sub>3</sub>, solar cells

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