Adjusting Interfacial Chemistry and Electronic Properties of Photovoltaics Based on a Highly Pure Sb$_2$S$_3$ Absorber by Atomic Layer Deposition

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Supporting Information

ABSTRACT: The combination of oxide and heavier chalcogenide layers in thin film photovoltaics suffers limitations associated with oxygen incorporation and sulfur deficiency in the chalcogenide layer or with a chemical incompatibility which results in dewetting issues and defect states at the interface. Here, we establish atomic layer deposition (ALD) as a tool to overcome these limitations. ALD allows one to obtain highly pure Sb$_2$S$_3$ light absorber layers, and we exploit this technique to generate an additional interfacial layer consisting of 1.5 nm ZnS. This ultrathin layer simultaneously resolves dewetting and passivates defect states at the interface. We demonstrate via transient absorption spectroscopy that interfacial electron recombination is one order of magnitude slower at the ZnS-engineered interface than hole recombination at the Sb$_2$S$_3$/P3HT interface. The comparison of solar cells with and without oxide incorporation in Sb$_2$S$_3$, with and without the ultrathin ZnS interlayer, and with systematically varied Sb$_2$S$_3$ thickness provides a complete picture of the physical processes at work in the devices.

KEYWORDS: atomic layer deposition, extremely thin absorber, antimony sulfide, transient absorption, interfacial layer, ultrathin layer

INTRODUCTION

The prospect of generalized energy conversion from sunlight demands that solar cells be engineered from stable, sustainable, nontoxic semiconductors based on earth-abundant elements. These requirements have been particularly hard to meet for the light absorbing layer in thin film p-n or p-i-n photovoltaics while maintaining decent performance. The optical and electronic properties of several heavier chalcogenides that do not fulfill these requirements (such as Cd$_x$Cu$_{1-x}$In$_2$Ga$_2$E$_2$, and PbE, E = S, Se, Te) have been extensively investigated.$^{1-7}$ More recently, materials such as Cu$_2$ZnSnE$_4$, lead-free perovskites, or Sb$_2$E$_3$ have been considered as attractive alternatives to the classical chalcogenides since they not only display appropriate physical properties for potential applications in solar cells devices but also have desirable environmentally friendly characteristics.$^{8-15}$ Those of them used in a p-i-n configuration have in common the necessity to be combined with a wide-bandgap electron conductor, which is typically an oxide (most prominently TiO$_2$) and often poorly bonds to the heavier chalcogenides, resulting in issues of physical and chemical nature (coordinationally unsaturated atoms and ions behave as recombination centers for charge carriers and dewetting of the heavy chalcogenides expose deleterious direct contacts between p and n layers, respectively). These issues represent barriers to the substitution of classical materials in thin-film photovoltaics with abundant and nontoxic alternatives.

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TiO₂ nanoparticles have been incompletely coated by Sb₂S₃ upon annealing and crystallization. This dewetting that occurs at the interface may have two different causes. In some cases, this dewetting hints at a poor chemical compatibility between the oxide of a hard, oxophilic metal ion and the suliothermic ion. This mismatch may also be related to the presence of deleterious trap states at even morphologically perfect TiO₂/Sb₂S₃ interfaces.

Therefore, interface engineering will play a key role in minimizing interface recombination, thereby increasing V_oc and FF. In fact, interfacial layers based on Inₓ(OH)ₓS₃ moieties have been used in order to avoid oxidation of Sb₂S₃ at the TiO₂/Sb₂S₃ interface. Subsequently, TiO₂ surfaces have also been treated with Mg, Al, and Ba, resulting in an enhancement of the energy conversion efficiency. A related approach, 1-decyl phosphonic acid has also been proven to effectively block the exposed TiO₂ areas. ZrO₂ and ZnS have been used as blocking layers to increase recombination lifetimes by passivating the interface, whereas very recently, Cs₂CO₃ has been found to reduce the series resistance of a TiO₂ compact layer by reducing its roughness and matching its conduction band energy to that of Sb₂S₃. In a complementary approach, the bulk properties of Sb₂S₃ have been optimized as well. Its n-type doping with Zn and Ti has been exploited to shift its Fermi level upward and has represented the best method so far to increase the overall energy conversion efficiency.

Recombination at the Sb₂S₃ interfaces with hole and electron transporter materials has been the subject of a very small number of fundamental studies shedding light on the factors defining the performance of these types of solar cells. These studies have considered either CBD-derived Sb₂S₃ or discontinuous Sb₂S₃ layers (or both). In the former case, the composition of the sulfoide layer offers limited control, and in the latter one, recombination can occur at various interfaces since the quantum dots or the dewetted layer does not fully separate p and n semiconductors. In both cases, the presence of unknown parameters limits the insight provided by the fundamental experimental work.

Thus, these recent papers highlight the need to completely eliminate oxygen from stibnite crystals, to improve the morphology of the Sb₂S₃ coatings, and to adjust both the chemical and physical properties of the stibnite/titania interface.

In this work, we use ALD to grow Sb₂S₃ as the photoactive layer and we compare oxygen-incorporating (Sb₂S₃₋ₓOₓ) and highly pure Sb₂S₃ phases. We characterize the composition and structure of the oxygen-incorporating and highly pure Sb₂S₃.
comprehensively. Further, we introduce a ZnS layer at the TiO$_2$/$\text{Sb}_2\text{S}_3$ interface to avoid dewetting of $\text{Sb}_2\text{S}_3$ and to minimize recombination. We determine photoexcited carrier dynamics by ultrafast transient absorption spectroscopy. Finally, we systematically optimize the thickness of the $\text{Sb}_2\text{S}_3$ light absorber layer in FTO/TiO$_2$/ZnS/$\text{Sb}_2\text{S}_3$/P3HT/PE-DOT:PSS/Au solar cells.

### RESULTS AND DISCUSSION

#### ZnS Interfacial Layer to Eliminate Dewetting of $\text{Sb}_2\text{S}_3$ on TiO$_2$

Dewetting of $\text{Sb}_2\text{S}_3$ on TiO$_2$ has been frequently reported in the literature, with varying degrees of gravity.\textsuperscript{20,22,28,32,39−41} In the case of our ALD-deposited highly pure $\text{Sb}_2\text{S}_3$, dewetting upon thermal annealing results in a complete deterioration of the conformal coating. Figure 1 compares the results of $\text{Sb}_2\text{S}_3$ layer annealing on TiO$_2$-coated fluorine-doped tin oxide (FTO) substrates as observed by scanning electron microscopy (SEM). $\text{Sb}_2\text{S}_3$ without oxide incorporation results in a loss of film continuity and major morphology change upon annealing (Figure 1a).

A heterogeneous surface with areas of varying severity of dewetting can be observed, leaving large portions of the FTO/TiO$_2$ substrate exposed. This leads to direct TiO$_2$/P3HT contact, which is deleterious for device performance. On substrates that feature a smoother surface, such as TiO$_2$-covered indium tin oxide (ITO), this effect is even more pronounced (Figure S1). We also observe that the incorporation of oxide into the $\text{Sb}_2\text{S}_3$ layer, achieved by introducing minute levels of O$_2$ into the inert gas used for ALD, suppresses dewetting altogether (Figure 1b). We note that the ALD growth rate, and therefore the layer thicknesses, is not affected significantly by the additional incorporation of oxide. This observation explains why the magnitude of the dewetting effect reported in various papers has been heterogeneous. In fact, based on the limited information available, there seems to be a correlation in the literature between a high degree of $\text{Sb}_2\text{S}_3$ purity and a prominent dewetting issue. Since the incorporation of oxide into $\text{Sb}_2\text{S}_3$ results in the formation of defects that limit the photovoltaic performance,\textsuperscript{22−28} it cannot be exploited as a satisfactory solution to the dewetting problem. However, the introduction of an ultrathin ZnS layer (15 ALD cycles or approximately 1.5 nm thickness) effectively suppresses this phenomenon (Figure 1c). In contrast to $\text{Sb}_2\text{S}_3$−O$_2$, the $\text{Sb}_2\text{S}_3$ layer on ZnS retains a certain plasticity during annealing, leading to the formation of large grains while conserving film continuity (Figure S2a). This grain growth is enhanced on the smoother ITO/TiO$_2$ substrates (Figure S2b) with respect to FTO/TiO$_2$. Thus, adhesion enhancement by ZnS is compatible with a significant mobility of atoms within the solid.

The question of whether the ZnS layer is preserved after the structural rearrangements caused by annealing can be addressed by a depth profile element analysis obtained by secondary ion mass spectrometry (SIMS, Figure 2). The essentially identical SIMS profiles obtained before and after annealing confirm that the ZnS layer remains as an ultrathin interfacial layer between the $\text{Sb}_2\text{S}_3$ and TiO$_2$ layers. Heating to 300 °C for 30 min does not cause diffusion of Zn into the $\text{Sb}_2\text{S}_3$ layer to any significant extent, which would generate a bulk or gradient doping and potentially affect performance.\textsuperscript{28} Note that the absolute increase of Sb signal observed at higher depth is due to the matrix effect; the proximity of the underlying oxide surface affects ion yields. Thus, this higher signal does not reflect the physical reality of the solid composition. The relevant observation here is the absence of any significant difference in the depth distribution of elements between the two samples.

#### Verifying the Purity of $\text{Sb}_2\text{S}_3$ Deposited by ALD

The structural identity and chemical purity of the ALD-grown ZnS/$\text{Sb}_2\text{S}_3$ layers (as compared to ZnS/$\text{Sb}_2\text{S}_3$−O$_2$) are characterized after thermal annealing by grazing incidence X-ray diffraction (GIXRD) and by Raman and X-ray photoelectron (XPS) spectroscopies. GIXRD diffractograms display all major peaks expected of the stibnite $\text{Sb}_2\text{S}_3$ phase (Figure 3a). Only one peak is observed beyond them, a signal that is easily attributed to the FTO substrate.

Raman spectra for both $\text{Sb}_2\text{S}_3$ and $\text{Sb}_2\text{S}_3$−O$_2$ thin films are analyzed in Figure 3b, together with spectral deconvolution to Lorentzian peaks the positions of which are labeled above the graphs. All signals generated by the oxide-free $\text{Sb}_2\text{S}_3$ (Figure 3b, upper panel), located at 157, 191, 207, 238, 282, 301, and 313 cm$^{-1}$ (black dashed lines), can be assigned to the stibnite phase.\textsuperscript{39,53−57} As specified in Table S1. The spectrum of $\text{Sb}_2\text{S}_3$−O$_2$ (Figure 3b, lower panel) reveals a line broadening in the regions near 240 cm$^{-1}$ and 280−320 cm$^{-1}$ that can be deconvoluted with the addition of higher-wavenumber bands associated with the vibrations of lighter nuclei. The new bands are centered at 246, 288, 305, and 317 cm$^{-1}$ (red dashed lines in Figure 3b) and can be ascribed to the oxide content (Table S1), in addition to stibnite, which is still the predominant phase.

To further confirm the composition of the $\text{Sb}_2\text{S}_3$ and $\text{Sb}_2\text{S}_3$−O$_2$ we conducted XPS analysis (Figure 3c−f and Figure S3). The $\text{Sb}$ 3d and S 2p regions of $\text{Sb}_2\text{S}_3$ (Figure 3c, e) are each dominated by one clean spin−orbit split doublet with maxima at 529.8 and 539.2 eV and at 161.6 and 162.8 eV, respectively. The atomic ratio S/Sb determined in the $\text{Sb}_2\text{S}_3$ phase is 1.43, confirming a near-perfect stoichiometry of ALD-deposited $\text{Sb}_2\text{S}_3$. A small contribution by oxygen-bonded Sb is found at 530.7 and 540.3 eV and is caused by exposure of the absorber layer surface to air upon transfer to the XPS chamber.\textsuperscript{25} The quantification reveals a ratio of 94% sulfur-bonded Sb to 6% oxygen-bonded Sb within the depth analyzed by XPS. The O 1s signal is found at 532.7 eV in Figure 3c. The $\text{Sb}_2\text{S}_3$−O$_2$ film exhibits significantly increased levels of oxygen, as observed both in the O 1s region and the Sb 3d signals (Figure 3d). The S 2p peaks reveal that sulfur in this oxide-containing solid is still present as sulfide exclusively (Figure 3f). For $\text{Sb}_2\text{S}_3$−O$_2$, the Sb 3d peak areas yield a composition of...
57% sulfide to 43% oxide. The S/Sb atomic ratio correspondingly drops to 0.95 only for Sb$_2$S$_3$$_{-x}$O$_x$. These results are in line with those obtained from Raman spectroscopy.

**Effects of Purity and ZnS Interfacial Layer on Photovoltaic Performance.** The incorporation of oxide into the Sb$_2$S$_3$ semiconductor has consequences on its physical properties. Ultraviolet photoelectron spectroscopy (UPS) is used to determine values for the work function (which is equivalent to the Fermi energy $E_F$), the energy of the valence band maximum ($E_{VB}$, or ionization energy), and the conduction band minimum ($E_{CB}$, or electron affinity). $E_F$ is obtained by subtracting the high binding energy cutoff from the photon energy ($h\nu = 21.2$ eV for He I radiation) of the UPS spectra (corrected by the −5 V applied bias). $E_{VB}$ is calculated as the sum of the Fermi energy and the lower binding energy onset in the UPS spectrum. Finally, subtracting $E_{VB}$ from the bandgap energy (1.7 eV for Sb$_2$S$_3$) yields $E_{CB}$.

The UPS spectra of the Sb$_2$S$_3$ and Sb$_2$S$_3$_{-x}$O$_x$ layers are presented in Figure 4a. The curve obtained for Sb$_2$S$_3$ (green shade) displays straight segments defining the onset and cutoff at 1.1 and 17.2 eV, respectively. These numbers allow us to calculate $E_F = 4.0$ eV (with respect to the vacuum level), $E_{VB} = 5.1$ eV, and $E_{CB} = 3.4$ eV. The Fermi energy level is slightly above the midgap (0.6 eV below $E_{CB}$) but is very close to it, which indicates that Sb$_2$S$_3$ is very close to being perfectly intrinsic, in line with the high level of stoichiometry observed by chemical analyses. The UPS spectrum for Sb$_2$S$_3$_{-x}$O$_x$ (blue shade in Figure 4a) shows a nonideal curve shape with a shoulder on the high binding energy side and no linear segment on the low-energy side. These observations may be related to the chemical heterogeneity of the solid and hinder any quantitative analysis.
The photovoltaic stack investigated for this thin film heterojunction cell is presented in Figure 4b and 4c. We use Sb$_2$S$_3$ as the central, intrinsic, light absorber material and complement it with n-type TiO$_2$ and p-type P3HT/ PEDOT:PSS as electron and hole transport materials (ETM, HTM), respectively. The contacts are FTO on the frontside and Au on the back. The Sb$_2$S$_3$ CB position of 3.4 eV determined by UPS confirms that ZnS represents a barrier to electron transfer (ET) to n-type TiO$_2$ (as shown in Figure 4b). Thus, the ZnS layer must be ultrathin in order to allow for electron extraction by tunneling.

Indeed, current–voltage (J–V) curves and external quantum efficiency (EQE) spectra demonstrate that with oxygen-containing Sb$_2$S$_3$–O$_x$ even a 1.5 nm thin ZnS layer causes a decrease in the photovoltaic performance (blue curves in Figure 5a–c). Thus, in the absence of a significant influence on morphology, the primary effect of the ZnS presence is a deleterious one. In contrast to this, adding ZnS to the highly pure Sb$_2$S$_3$ results in an improvement of both short-circuit current density ($J_{sc}$) and $V_{oc}$ (green curves on Figure 5a,b,c) obtained with 54 nm Sb$_2$S$_3$. In the dark, the diode rectification is improved if Sb$_2$S$_3$ is rid of its oxide, and this improvement is further magnified in the presence of the ZnS layer (Figure 5b). The photovoltaic power conversion performance numbers obtained from a statistically significant sample batch (all of them based on a 54 nm thick light absorber layer) confirm this effect (Figure S5 and Figure S4). When Sb$_2$S$_3$–O$_x$ is the photoactive layer, the devices provide a decent average efficiency of 2.0%, with a $V_{oc}$ of 0.25 V, $J_{sc}$ of 9.9 mA cm$^{-2}$, and a FF of 0.39. However, when we introduce a ZnS interfacial layer of 1.5 nm, the average parameters drop to 1.3%, 0.47 V, 7.9 mA cm$^{-2}$, and 0.35, respectively. On the other hand, when we use Sb$_2$S$_3$ as a photoactive layer with high purity and stoichiometry, the interfacial layer is fundamental to preserving a continuous layer after converting the amorphous phase to stibnite via thermal annealing. The devices fabricated with Sb$_2$S$_3$ without ZnS leave significant areas of TiO$_2$ exposed (Figure 1a) in direct contact with P3HT. However, introducing 1.5 nm of ZnS on the interface between TiO$_2$ and Sb$_2$S$_3$ avoids dewetting, resulting in a significant improvement of the photovoltaic parameters. These devices provide an average efficiency of 3.4%, $V_{oc}$ of 0.62 V, $J_{sc}$ of 13.4 mA cm$^{-2}$, and FF of 0.40. In other words, they outperform both the Sb$_2$S$_3$-based cells without ZnS and their oxide-containing counterparts by 60%.

**Charge Carrier Dynamics.** To gain more insight into the charge carrier dynamics governing the solar cell operation, transient absorption (TA) spectroscopy was performed on four samples based on ZnS (1.5 nm)/Sb$_2$S$_3$ (54 nm) and associated with different charge-selective layers of the full cell. These configurations allow us to attribute time scales observed experimentally to the dynamics of certain carrier types, and they include:

- (A) ZnS/Sb$_2$S$_3$ (both $h^+$ and $e^-$ pathways blocked);
- (B) TiO$_2$/ZnS/Sb$_2$S$_3$ (only $e^-$ pathway open);
- (C) ZnS/Sb$_2$S$_3$/P3HT (only $h^+$ pathway open); and
- (D) TiO$_2$/ZnS/Sb$_2$S$_3$/P3HT (both $h^+$ and $e^-$ pathways open).

The representative TA spectra showing the spectral evolution of the transient signal over the first 5 ns are shown in Figure S5. The data are clearly distinct for the four different configurations, and they result from more than just one exponentially decaying species. Therefore, we performed a global analysis fitting to extract the individual components of the time evolution as decay-associated difference spectra (DADS), presented for each configuration in Figure 6, and

![Figure 5. Effects of oxygen incorporation into Sb$_2$S$_3$ (54 nm) and of the ZnS interfacial layer on (a) the J–V characteristics on a linear current scale, (b) the dark J–V curves on a logarithmic current scale, (c) the EQE spectra for four representative samples, and (d) average power conversion efficiencies.](image)

![Figure 6. Decay-associated difference spectra and their associated lifetimes obtained from the transient absorption signal presented for (a) ZnS/Sb$_2$S$_3$, (b) TiO$_2$/ZnS/Sb$_2$S$_3$, (c) ZnS/Sb$_2$S$_3$/P3HT, and (d) TiO$_2$/ZnS/Sb$_2$S$_3$/P3HT.](image)
The CT process. A new spectrum (DADS2, green) with weak but is slightly longer, as ET through the tunneling barrier slows initially, characterized by the interpretation is that the intermediate state represents the ground state with a lifetime of 10.3 ns. The most logical on a time scale of 1.7 ps, and the intermediate decays back to line). The excited state conversion to this intermediate occurs generated as a result of ET on a time scale similar to case lifetime of 14.4 ns.

The samples containing only Sb$_2$S$_3$ and ZnS (configuration A) produce two DADS components (Figure 6a), whereas the samples containing either the electron or hole transporting layers (or both together) yield three components. The additional DADS are rationalized by and interpreted using the introduction of the $h^+$ and $e^−$ pathways accessible as various material layers are added. When only ZnS/Sb$_2$S$_3$ is present, the DADS reveal the decay of the excited state (Sb$_2$S$_3^*$) generated initially, characterized by the $≈710$ nm absorption (red line), concomitant with the growth of an intermediate state with its main feature at 570 nm (and a shoulder at $≈680$ nm, blue line). The excited state conversion to this intermediate occurs on a time scale of 1.7 ps, and the intermediate decays back to the ground state with a lifetime of 10.3 ns. The most logical interpretation is that the intermediate state represents $e^−$ and $h^+$ carriers separated within the material from the initially formed exciton.

In configuration B (TiO$_2$/ZnS/Sb$_2$S$_3$), in which only $e^−$ transfer to the n-type material is accessible, the data produce three DADS components (Figure 6b). DADS1 (the exciton that produces $e^−$ and $h^+$ carriers within the material) has red-shifted spectral features (650 nm instead of 570 nm, red line) with respect to configuration A, indicating that charge-transfer species are involved. Instead of representing only the $h^+$ and $e^−$ in Sb$_2$S$_3$, this DADS1 represents formation of free carriers and subsequent charge transfer to TiO$_2$. The first intermediate is generated as a result of ET on a time scale similar to case A, but is slightly longer, as ET through the tunneling barrier slows the CT process. A new spectrum (DADS2, green) with weak positive features at around 600–640 nm and 710–750 nm represents the electron located in the TiO$_2$ layer. DADS2, then, represents back-transfer of the electron from TiO$_2$ to Sb$_2$S$_3$ with a time constant of 5 ns to yield a spectrum (DADS3, blue) that shows similar spectral features to the separated carriers within the Sb$_2$S$_3$ phase (DADS1 in A) which then recombines to the ground state with essentially the same lifetime of 14.4 ns.

Figure 6c shows the DADS obtained from configuration C (ZnS/Sb$_2$S$_3$/P3HT), in which only $h^+$ transfer is assessable. Similarly to configuration B, which introduced an $e^−$ transfer pathway, three DADS are produced upon analysis when only the $h^+$ transfer pathway is operative. In line with configurations A and B, DADS1 of configuration C shows the excited state decay with a fast time component of 1.1 ps, due to exciton dissociation and $h^+$ transfer to P3HT. In a similar fashion to configuration A, the spectral features of the DADS1 spectrum (red line) show the decay of an excited state at $≈700$ nm concomitant with formation of the $e^−$/$h^+$ pair state as negative features at $≈550$ nm and $≈600$ nm. The subsequent component is spectrally distinct from the intermediate state (the 5 ns DADS2) formed for configuration B, indicating that the green spectrum in configuration C represents the $h^+$ transfer state. Further, this intermediate DADS2 decays with a smaller time constant of 0.1–0.5 ns, indicating that the $h^+$ back-transfer is substantially faster than the analogous $e^−$ transfer process. The third state (blue curve DADS3, trapped state in Sb$_2$S$_3$ upon $h^+$ return) recovers to the ground state with a time constant of 9.9 ns in the final DADS3 spectrum.

In configuration D (TiO$_2$/ZnS/Sb$_2$S$_3$/P3HT), both $e^−$ and $h^+$ transfer to the respective charge-selective layers are possible (Figure 6d). However, both the DADS spectra and their corresponding time constants for configuration D are most comparable to those of configuration C. This is logical inasmuch as the faster process, that is, the transfer and back-transfer of $h^+$, dominates the excited-state dynamics in the full photovoltaic stack.

Taken together, the transient absorption spectra suggest an overall picture of the excited-state dynamics of this p-i-n heterojunction shown schematically in Figure 7. The ZnS-mediated junction between the light absorber Sb$_2$S$_3$ and the electron conductor TiO$_2$ is of sufficient quality, such that the main factor causing recombination is the interface between Sb$_2$S$_3$ and P3HT. Thus, TA spectroscopy reveals that one factor limiting device performance is this recombination, which primarily affects $V_{oc}$. Of course, the other main aspect to be considered is light absorption, which mostly influences $J_{sc}$.

**Optimization of Absorber Layer Thickness.** In order to maximize the generation and extraction of charge carriers, it is crucial to optimize the thickness of the Sb$_2$S$_3$ layer. Representative J-V curves of FTO/TiO$_2$/ZnS/Sb$_2$S$_3$/HTM/ Au solar cells based on five different Sb$_2$S$_3$ thicknesses (600, 900, 1200, 1500, and 2700 ALD cycles, corresponding to 36, 54, 72, 90, and 162 nm) are shown in Figure 8a. The average values of the photovoltaic parameters obtained on several nominally identical samples of each type are presented in Figure 8b and Figure S6. All data indicate that the optimal thickness is on the order of about 54 to 72 nm, yielding average efficiencies of 3.4% with a $V_{oc}$, $J_{sc}$, and FF values of 620 mV, 13.5 mA cm$^{-2}$, and 0.41, respectively, for 54 nm. Both thinner and thicker Sb$_2$S$_3$ layers result in lower performance parameters.

EQE measurements allow us to identify the factors limiting performance on either side of the optimal Sb$_2$S$_3$ thickness (Figure 8c). Devices with 36 nm of Sb$_2$S$_3$ exhibit incomplete absorption of long wavelengths in UV-visible absorption

Figure 7. Schematic representation of the excited-state dynamics of the TiO$_2$/ZnS/Sb$_2$S$_3$/P3HT junction.
Thus, layers with the high-energy photons generate carrier pairs near the Sun—underlying oxide electron transport material. For the homogeneous absorption, the quality of Sb2S3 and the quality of its interface with the transport material. For longer wavelengths, the EQE remains maximal; a more homogeneous absorption throughout the layer. In thick Sb2S3 layers, most of the optical absorption is due to the lower extinction coefficient, mirrored in a decay of EQE starting from 500 nm. This loss mechanism is reduced for the 54 and 72 nm samples, which optimize the absorption profile and EQE spectrum in the red (just beyond the bandgap of 1.7 eV). Starting with the 72 nm sample, however, a distinct phenomenon is observed, namely, an EQE loss in the blue region of the spectrum. At those short wavelengths, large extinction coefficients ensure that all light is absorbed, but in fact, the thicker the layer is, the less homogeneous the absorption is. In thick Sb2S3 layers, most of the high-energy photons generate carrier pairs near the sun-facing side of the absorber, that is, near its interface to ZnS/TiO2. Thus, layers with ~72 nm thickness become limited by the diffusion length of holes generated from short-wavelength photons (~550 nm), which no longer suffices to reach the hole transport material. For longer wavelengths, the EQE remains maximal; a more homogeneous absorption throughout the Sb2S3 layer renders the effect less severe given that a smaller fraction of carriers has to be transported across the full layer thickness.

## CONCLUSIONS

Taken together, these results provide a detailed picture of how the quality of Sb2S3 and the quality of its interface with the underlying oxide electron transport material affect the physical parameters and the functional performance. For the first time, and in contrast to previous studies based on a heavier chalcogenide light absorber that was oxygen contaminated, sulfur deficient, and/or present as a discontinuous layer, the present data are valid for highly pure, stoichiometric, and conformal ALD-grown Sb2S3 layers on TiO2. They unveil the fundamental excited-state dynamics of a TiO2/ZnS/Sb2S3/P3HT system. The high purity of our absorber layers is proven by Raman and XPS analyses. The introduction of an ultrathin (1.5 nm) ZnS layer by ALD reduces the undesired dewetting during annealing that occurs with oxide-free Sb2S3 and passivates the surface defects at the interface. Solar cells based on this ZnS/Sb2S3 material system outperform not only their oxygen-containing counterparts but also the ZnS-free devices by approximately 60%. A systematic transient absorption spectroscopy study reveals the limiting nature of recombination at the Sb2S3/P3HT interface. The study discloses that in the presence of the ultrathin ZnS layer, the deleterious back-transfer of electrons from TiO2 to Sb2S3 occurs within 5 ns, which is much slower than the corresponding process for holes (<0.5 ns at Sb2S3/P3HT). This study provides a highly well-defined model system in which to study the effects of geometric parameters on device performance systematically. In particular, we were able to identify the optimal Sb2S3 absorber layer thickness in an unambiguous manner, minimizing transport and recombination losses.

One logical route to follow up on these results will be the generation of nanostructured interfaces to mediate this trade-off. Another would be the improvement of the Sb2S3/HTM interface. These and other directions of research are currently being explored in our laboratory. More generally, our results may provide avenues for combining heavier chalcogenide light absorbers with wide-bandgap oxide carrier-selective layers, which could present opportunities for replacing some of the materials currently used in classical thin film photovoltaics with stable and nontoxic oxides of abundant metals as alternatives.

## EXPERIMENTAL SECTION

**Sample Preparation.** Glass and FTO substrates (sheet resistance 10 Ω/sq, Technistro) were cleaned by sonication for 5 min each in acetone, isopropanol, and deionized water. For SIMS and some of the SEM images, smooth homemade ITO films with a thickness of 300 nm were prepared by RF magnetron sputtering on glass substrates from an In2O3/SnO2 target (90:10, 99.5%) at a power density of 1 W cm−2 with a working pressure of 4.3 Pa and an Ar flow of 5 sccm (CRC 622 model, Torr International, Inc.). The base pressure was 1.3 × 10−6 Pa. Similarly, a TiO2 blocking layer with a thickness of 50 nm was deposited from a TiO2 target (99.99%) at a higher power density of 2.5 W cm−2. The substrates were then annealed at 450 °C for 2 h in air to convert the amorphous TiO2 to anatase phase. ZnS and Sb2S3 (or Sb2S3...Ox) were deposited in a homemade hot-wall ALD. The precursors used were diethylzinc (95%, abcr), tris(dimethylamido)-antimony(III) (Sb(NMe2)3, 99.99%, Sigma-Aldrich), H2S (3% vol in N2, Air Liquide), and O2 (0.5% vol in N2, Air Liquide), and O2 (0.5% vol in N2, Air Liquide). Nitrogen was used as the carrier gas. Pulse, exposure, and purge time were set to 0.2, 15, and 15 s, respectively, in all cases, except for Sb(NMe2)3, for which the pulse time was 1.5 s. The Sb precursor was kept at 40 °C, and the chamber temperature was 150 °C for ZnS and 120 °C for Sb2S3 deposition. Deposition of Sb2S3 on ZnS was carried out in the same reactor without breaking vacuum. Amorphous Sb2S3 is converted to the stibnite phase by annealing the samples on a hot plate in an Ar glovebox at 300 °C for 30 min. Then, 15 mg of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate (PEDOT:PSS, HTL Solar, Osaka) was spin coated at 6000 rpm for 60 s. The samples were then dried in an N2 glovebox at 90 °C for 30 min. Subsequently, poly(3,4-ethylenedioxythiophene) poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate (PEDOT:PSS, HTL Solar, Osaka) was spin coated at 6000 rpm for 60 s. The samples were treated at 90 °C for 30 min in an N2 glovebox. Finally, a 100 nm layer of Au (Au target, 99.99%) was deposited as a top contact by DC sputtering at 12.7 Pa with an Ar
flow of 30 sccm and a power density of 0.7 W cm$^{-2}$, using a shadow mask to deposit electrodes of 0.1 cm$^2$.

**Characterization.** Photovoltaic characterization was performed with a solar simulator (Newport) using a Xe lamp source calibrated to AM1.5 at 100 mW cm$^{-2}$ with a reference Si solar cell (Newport). EQE was measured using a system (Oriel’s QEPSpec-b) equipped with a 300 W Xe light source, a monochromator, and a lock-in amplifier. The electrical data were recorded by a single-channel Gamry Reference 600 instrument. Steady-state optical absorption spectra were measured with an ultraviolet-visible spectrophotometer (Ocean Optics) equipped with a DH-2000-L light source, a HR40000 spectrometer, and an ISP-50-8-R integrating sphere. The absorption spectra were obtained by subtracting the transmitted and reflected/scattered intensities from the incident intensity. SEM micrographs were recorded with a JEOl JSM 6400 instrument equipped with a LaB$_6$ cathode and an EDX detector from SAMx or a Gemini 500, Carl Zeiss field-emission instrument. GIXRD was performed on a Bruker D8 Advance equipped with a Cu Kør source and a LynxEye XE T detector. Thicknesses of ALD layers were determined by spectroscopic ellipsometry using a SENpro by Sentech.

Raman measurements were performed with a LabRam HR800 (Horiba Jobin Yvon) instrument equipped with a BX-41 (Olympus) microscope. Raman spectra were recorded in backscattering geometry with 1200 gr mm$^{-1}$ diffraction and a He–Ne gas laser (632.8 nm wavelength). The laser power at the sample was about 2 mW under a 20 μm objective (N.A. = 0.4). The diameter of the coherent part was 100 μm. The accumulation time was 180 s with 10 repetitions. The spectra were deconvoluted into bands of Lorentzian shape based on the high crystalline quality of the samples.

The XPS and UPS analyses were carried out using a combined auger, X-ray, and ultraviolet photoelectron spectrometer (Thermo Fisher Scientific, ESCAlab 250Xi) with monochromatic Al Kα radiation (photon energy = 1486.6 eV). The total energy resolution was about 0.55 eV. XPS spectra were recorded in the constant pass energy mode at 50 eV, using an X-ray spot size of 650 μm. Investigations were carried out at ambient temperature in UHV with a pressure on the order of 1 × 10$^{-9}$ mbar. As a radiation source for UV spectroscopy, a UV lamp with the He I line (photon energy = 21.2 eV) was used. The total energy resolution was about 0.4 eV.

Depth profiles of the samples were recorded using a SIMS instrument of the sector-field type (Cameca ims 6f). The primary ion beam consisted of 2.5 keV O$_2^+$ ions with a 4.5 nA current, which was scanned over an area of 300 μm × 300 μm. Positive secondary ions were detected from the inner 150 μm (diameter) of the sputter crater. The mass resolution was set to a low value (300) to ensure a high transmission.

TA spectroscopy was performed with an Ultrafast Systems Helios spectrometer on the following four samples: (A) glass/ZnS/Sb$_2$S$_3$, (B) glass/FTO/TiO$_2$/ZnS/Sb$_2$S$_3$, (C) glass/ZnS/Sb$_2$S$_3$/P3HT, and (D) glass/FTO/TiO$_2$/ZnS/Sb$_2$S$_3$/P3HT. Pulses of laser light of 150 fs duration and 800 nm wavelength were generated with a Coherent Libra amplified Ti/sapphire system at 1.3 W and 1 kHz repetition rate. Approximately 80% of the 800 nm pulses was sent to a Topas-C optical parametric amplifier to generate a 480 nm pump pulse. The pump pulse was passed through a depolarizing optic to eliminate contributions to the TA signal from orientational diffusion and was attenuated to between 0.5 mW and 1 mW to prevent decomposition of the sample. The remainder (~20%) of the 800 nm light was sent through a sapphire crystal to generate a white light continuum for use as the probe pulse. The referencing was accomplished by subtracting the ΔA spectrum calculated for the reference channel from the ΔA spectrum calculated for the probe channel, for each pump-on/pump-off pair of the probe pulses. The TA spectra were measured over a 5 ns window. For each scan, 250 time points were recorded with exponential time spacing, and each sample was subjected to three scans. Data analysis was performed by extracting and retaining 2–3 principal components and fitting using global analysis software (Ultrafast Systems Surface Xplorer) to isolate DADS and their corresponding lifetimes. The number of principal components and DADS chosen when fitting the data set of each configuration was selected to obtain the lowest error value provided by the Surface Xplorer software (i.e., the value of $\chi^2$ that was closest to 1).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.9b01721.

(Figure S1) SEM micrographs of highly pure Sb$_2$S$_3$ without and with a ZnS interfacial layer; (Figure S2) XPS surveys for Sb$_2$S$_3$ and Sb$_2$S$_3$–O$_x$; (Table S1) Raman band center positions observed experimentally and assignments with symmetry and phonon mode descriptions; (Figure S3) open circuit current, short circuit current, fill factor, and efficiencies for the different solar cell devices; (Figure S4) transient absorption spectra for each of the four semiconductor stack configurations; and (Table S2) summary of lifetimes obtained for each DADS of each configuration (PDF)

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Notes

The authors declare no competing financial interest.

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