Conduction Band Energy-Level Engineering for Improving Open-Circuit Voltage in Antimony Selenide Nanorod Array Solar Cells

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Antimony selenide (Sb$_2$Se$_3$) nanorod arrays along the [001] orientation are known to transfer photogenerated carriers rapidly due to the strongly anisotropic one-dimensional crystal structure. With advanced light-trapping structures, the Sb$_2$Se$_3$ nanorod array-based solar cells have excellent broad spectral response properties, and higher short-circuit current density than the conventional planar structured thin film solar cells. However, the interface engineering for the Sb$_2$Se$_3$ nanorod array-based solar cell is more crucial to increase the performance, because it is challenging to coat a compact buffer layer with perfect coverage to form a uniform heterojunction interface due to its large surface area and length–diameter ratio. In this work, an intermeshing In$_2$S$_3$ nanosheet-CdS composite as the buffer layer, compactly coating on the Sb$_2$Se$_3$ nanorod surface is constructed. The application of In$_2$S$_3$-CdS composite buffers build a gradient conduction band energy configuration in the Sb$_2$Se$_3$/buffer heterojunction interface, which reduces the interface recombination and enhances the transfer and collection of photogenerated electrons. The energy-level regulation minimizes the open-circuit voltage deficit at the interfaces of buffer/Sb$_2$Se$_3$ and buffer/ZnO layers in the Sb$_2$Se$_3$ solar cells. Consequently, the Sb$_2$Se$_3$ nanorod array solar cell based on In$_2$S$_3$-CdS composite buffers achieves an efficiency of as high as 9.19% with a $V_{OC}$ of 461 mV.

1. Introduction

Photovoltaic (PV) technologies that directly convert solar radiation into electricity, offer a green and renewable energy to meet the growing demand in the developed world. Among thin film solar cells, great successes have been achieved in copper indium gallium selenide (CIGS), cadmium telluride (CdTe), and perovskites with certified power-conversion efficiency (PCE) over than 22%.[1–4] However, the toxicity, natural instability, and limited abundance of some of their constituent elements might be the obstacles for large-scale application.[5,6] Thus, alternative earth-abundant light-absorbing materials have been investigated for high efficiency, eco-friendly, and stable solar cells.

Antimony selenide (Sb$_2$Se$_3$) has recently emerged as a promising PV absorber material and been receiving more and more research interest due to its favorable material and optoelectronic properties.[7–9] It exhibits proper bandgap of 1.1–1.3 eV, high absorption coefficient of $10^5$ cm$^{-1}$ in the visible region, excellent carrier mobility, and good device stability. [10,11] Moreover, Sb$_2$Se$_3$ is environmentally friendly, and is not in the list of highly materials by US, EU, or Chinese regulation authorities. The abundant of elements Sb and Se in the earth’s crust is 0.2 and 0.05 ppm, respectively.[7,11] Consequently, this makes Sb$_2$Se$_3$ a very promising absorber material for PV application.[12–14]

The most attractive merit of Sb$_2$Se$_3$ is the one-dimensional (1D) nanoribbon grain structure comprising of covalently bonded (Sb$_2$Se$_3$)$_n$ ribbons held together via Van der Waals forces.[15,16] This unique 1D crystal structure leads to not only the bond anisotropy but also the strongly anisotropy in optical, electrical, and defect properties. For instance, the hole mobility along ribbon (c-direction) is nearly four times than that cross the ribbons (b-direction).[16,17] Thus, control of the crystal orientation of Sb$_2$Se$_3$ grains is the very crucial to the quality of absorber layer and also the device performance of solar cells.[18,19] Tang’s group reported that the strong correction between device performance and the orientation of Sb$_2$Se$_3$ absorber layer.[13] The detailed analysis revealed that the carrier transport in the [221]-oriented grain
buffer reduces the recombination paths at the heterojunction interface, leading to an increase in recombination activation energy $E_r$ and $V_{OC}$. Moreover, a gradient conduction band maximum is formed for the In$_3$S$_3$/CdS composite layer, which is favorable for the transfer and collection of photogenerated electrons. As a result, a PCE of 9.19% is achieved for device based the optimized composite buffer with $V_{OC}$ of 461 mV, $J_{SC}$ of 29.92 mA cm$^{-2}$ and FF of 66.67%, while the PCE of the standard device with single CdS buffer is 7.39%.

2. Results and Discussion

As illustrated in Figure 1, in this work, the Sb$_2$Se$_3$ nanorod array (NRAs) were prepared by close spaced sublimation (CSS) technique by subliming the Sb$_2$Se$_3$ powder source onto the surface selenized Mo-coated glass substrate. The sublimation process continues for tens of seconds and the thickness of Sb$_2$Se$_3$ NRAs is about 1000–1200 nm. Afterward, the Sb$_2$Se$_3$ NRAs were first coated by solution-processed indium sulfide (In$_n$S$_x$) nanosheet layer, and followed by deposition of cadmium sulfide coating to get the In$_n$S$_x$/CdS composite buffers. We first check the morphologies and compositions of the In$_n$S$_x$/CdS composite layers, and the single In$_n$S$_x$ nanosheet layer and single CdS layer were also included for comparison. In this work, the In$_n$S$_x$ nanosheet layer and CdS layer were prepared by hydrothermal deposition and chemical bath deposition (CBD), respectively. The composite layers were controlled by tuning the CdS deposition time between 5 and 11 min, while keeping the In$_n$S$_x$ deposition condition was same for all samples. For description clarity, we denoted the sample coated with hydrothermal In$_n$S$_x$ and CdS buffer for 5 min as C5, and CBD CdS layer for 7, 9, and 11 min as C7, C9, and C11, respectively.

Figure 2 shows the top-view scanning electron microscope (SEM) images of Sb$_2$Se$_3$ NRAs coated with In$_n$S$_x$, In$_n$S$_x$/CdS composites (C5, C7, C9, C11), and single CdS buffer layers. Obvious nanosheet-like In$_n$S$_x$ films could be observed on the surface of Sb$_2$Se$_3$ nanorods after the hydrothermal deposition of In$_n$S$_x$, for 100 min (Figure 2a; and Figure S2a, Supporting Information), resulting in a dendritic Sb$_2$Se$_3$/In$_n$S$_x$ core/shell heterojunction. The X-ray diffraction (XRD) pattern (Figure S1, Supporting Information) indicates that the peaks can be indexed to pure cubic In$_n$S$_x$, phase (JCPDS 65-0459). After deposition of 5 min CdS, the dendritic features of the NRAs become weakened but remain loose nanorod surface (C5, Figure 2b). With further increase in the CBD reaction time to 9 (C9) and 11 min (C11), the dendritic NRAs disappears and dense and slightly rough surface formed on the Sb$_2$Se$_3$ nanorod (Figure 2e). In contrast, for the NRAs coated with single CBD CdS layer, a fully conformal and intact coating of CBD processed CdS layer on the Sb$_2$Se$_3$ NRAs are obtained, and maintains the smooth nanorod surface, as shown in Figure 2f.

This strongly difference in morphology could be ascribed to the different mechanism for the growth of CdS and In$_n$S$_x$. The formation of In$_n$S$_x$ nanoflakes is based on the slow release of $\text{In}^{3+}$ and $\text{S}^{2-}$ ions in an acidic solution, and the following nucleation and growth stages on the Sb$_2$Se$_3$ nanorod surface when the ionic product exceeds the solubility product, which is a typical ion-by-ion mechanism, ions, including $\text{In}^{3+}$, $\text{C}_6\text{H}_7\text{O}_7^{-}$ (L$^-$), $\text{S}^{2-}$, $\text{H}^+$ and other ions, were formed in the reaction aqueous solution by ionization and hydrolysis action from the precursors.

(translation within the covalently bonded (Sb$_2$Se$_3$)$_n$ nanoribbons) was much easier than in the [120]-oriented grains (charge hopping between ribbons held together by Van der Waals force). They further investigated the effect of ZnO substrate orientation on the quality of the top Sb$_2$Se$_3$ layer.[10] As a result, highly preferred [221] orientation Sb$_2$Se$_3$ absorber was obtained, and the corresponding superstrate ZnO/Sb$_2$Se$_3$ thin film solar cell demonstrated a high conversion efficiency and good stability under the test condition of International Electrochemical Commission 61 646 protocol.[10] Up to now, most reported Sb$_2$Se$_3$ solar cells are based on [221]-oriented Sb$_2$Se$_3$ absorber layer with excellent carrier transport property.[20–24] Recently, we reported the construction of photovoltaic devices based on Sb$_2$Se$_3$ nanorod arrays along the [001] direction, where the single crystal Sb$_2$Se$_3$ nanorod consisted of tilted (Sb$_2$Se$_3$)$_n$ nanoribbons stacked vertically on the substrate.[25] The [001]-oriented Sb$_2$Se$_3$ grain allows the carrier transport only in the covalently-bonded ribbons and is beneficial for device performance improvement. In addition, the growth of 1D [001]-oriented Sb$_2$Se$_3$ nanorod is thermodynamically favorable, and results in no dangling bonds at their grain boundaries (GBs) due to the low formation energies. The potential issue of carrier recombination loss at the GBs could be alleviated for the 1D Sb$_2$Se$_3$ nanorod-based solar cells, whereas the recombination through dangling bonds at the GBs is the main factor limiting the device performance for traditional 3D poly-crystalline thin film solar cells, such as CuInGaSe$_2$, CuInS$_2$, CdTe, CZTS, etc.[26] From this view, the interface recombination, especially occurs at the terminals of the single-crystal Sb$_2$Se$_3$ nanorod, become dominant for the performance improvement of Sb$_2$Se$_3$-based solar cells. The Sb$_2$Se$_3$ nanorod-based solar cells suffer from higher interface defect density and carrier recombination and thus have more serious open-circuit voltage deficit than the Sb$_2$Se$_3$ thin film configuration devices.[21,27–30] The element interdiffusion at the junction interface is another interesting feature of Sb$_2$Se$_3$/CdS heterojunction solar cells.[31,32] Williams et al. revealed that an atom scale interfacial layer can unavoidably form at the Sb$_2$Se$_3$/CdS interface due to the rapid interdiffusion of Sb and Se from Sb$_2$Se$_3$, which would increase the interfacial recombination and lead to low device efficiencies.[33] An ultrathin titanium oxide (TiO$_2$) layer deposited by atomic layer deposition (ALD) has been employed to passivate the Sb$_2$Se$_3$ nanorod array-based heterojunction interface, and an power conversion efficiency (PCE) as high as 9.2% was achieved.[21] The interface engineering was a crucial factor for high efficiency Sb$_2$Se$_3$ solar cells. Vacuum thermal evaporated buffer layer was also employed in the substrate Sb$_2$Se$_3$ devices with following chemical etching and annealing procedure.[34]

In this work, we propose a solution processed In$_3$S$_x$/CdS composite buffer layer application in Sb$_2$Se$_3$ nanorod array solar cells. This fabrication procedure is vacuum-free and low-cost in comparison with ALD-TiO$_2$ technique. Meanwhile, the band alignment structure of the heterojunction is another crucial factor that relating to the interface recombination behavior and determining the efficiencies of thin film solar cells. A cliff-like band offset is observed at the Sb$_2$Se$_3$/CdS interface, which would increase the interface recombination and thus decrease the device $V_{OC}$.[35] The band structure of In$_3$S$_x$/CdS composite buffer could be controlled by regulating the deposition of CdS layer. The composite...
(indium chloride, citric acid and TAA) in the aqueous solution. 
\( \beta \)-In\(_2\)S\(_3\) can be formed under a low concentration of \( S^{2-} \) due to its low solubility of \( 5.7 \times 10^{-74} \) \(^{[36]} \). Citrate ion \((C_6H_7O_7)^-\) combines with some of In\(^{3+}\) to reduce the concentration of free In\(^{3+}\) in an acidic solution (pH = 2). In\(_2\)S\(_3\) nuclei can be formed by directly combination of In\(^{3+}\) and S\(^{2-}\) under a low concentration. On the other hand, citrate ion could also be combined with some of In\(^{3+}\) to form the indium-citrate complex ion \( \text{In(C}_6\text{H}_7\text{O}_7)^-\)\(_3\), and play role in controlling the concentration of free In\(^{3+}\) in the solution. This allows the formation of In\(_2\)S\(_3\) nuclei on the Sb\(_2\)Se\(_3\) nanorod surface. Then the nuclei on the nanorod surface grow self-assembled and gradually to form nanoflakes due to the difference in surface energy of \( \beta \)-In\(_2\)S\(_3\).\(^{[36,38]} \)

In contrast, the formation of CdS layer is normally following a complex-decomposition cluster mechanism, which is based on the formation of an intermediate complex with the anion-forming reagent instead of reacting directly with a free anion.\(^{[37,39,40]} \) The growth of CdS occurs in an alkaline
solution consisting of ammonium hydroxide providing ammonia in the solution. The cadmium ions (Cd\(^{2+}\)), generated from the cadmium salt, complex with ammonia to form amino-cadmium complex ion Cd(NH\(_3\))\(_4\)\(^{2+}\), controlling the concentration of free cadmium ions. Then, Cd(NH\(_3\))\(_4\)\(^{2+}\) complex ion reacts with hydroxide ions to form the adsorbed dihydroxo-diammin-cadmium complex [Cd(OH)\(_2\)(NH\(_3\))\(_2\)]\(_{ads}\) on the In\(_2\)S\(_3\) flake or Sb\(_2\)Se\(_3\) nanorod surface. This complex then reacts with thiourea to form the metastable complex [Cd(OH)\(_2\)(NH\(_3\))\(_2\)SC(NH\(_2\))\(_2\)]\(_{ads}\). The final CdS was formed through decomposition of the metastable complex. In this stage, the formation of CdS is more likely an in situ and conformal growth process. Furthermore, as the reaction time prolonging, the CdS becomes bigger nanoparticles gradually and closer together to form continuous films, and the growth rate is high in this stage. This could explain that the huge difference in morphology for different deposition time of CdS, as shown in Figure 2. Insufficient deposition time of CdS (7 and 5 min) on the rough Sb\(_2\)Se\(_3\)/In\(_2\)S\(_3\) nanorod surface maintains the morphology of In\(_2\)S\(_3\) flake (Figure 2b–c). However, when the reaction time prolongs to 11 min or more, CdS could fill the space between the In\(_2\)S\(_3\) flakes, and results in a smooth surface.

**Figure 3**: and Figure S3 (Supporting Information) display the difference in morphology and composition in detail between the Sb\(_2\)Se\(_3\) NRAs coated with In\(_2\)S\(_3\) nanoflake films and with In\(_2\)S\(_3\)-CdS composite (C7) films. As shown, the surface of Sb\(_2\)Se\(_3\) nanorod is covered by a shell of nanoflake film, like prickly tree branches. High-magnification TEM image in Figure 3b shows the In\(_2\)S\(_3\) nanoflakes are tightly attached to the Sb\(_2\)Se\(_3\) nanorod surface, forming a core–shell nanorod structure. In contrast, after several minutes of deposition of CdS, the prickly-like nanorod surface became slightly smooth, as shown in Figure 3c,d. High-angel annular dark-field scanning transmission electron microscope (HAADF-STEM) equipped with energy dispersive spectroscopy (EDX) measurement was performed to characterize the composition of this core/shell nanorod structures. Single nanorod was chosen to analyze the Sb, Se, In, Cd, and S element distribution for the core/shell heterostructure and the results are shown in Figure 3f. It exhibits that the Sb and Se elements were distributed in the core, and the copresence of Cd, In, and S elements in the shell of the nanorod heterostructure. On the contrary, only In and S elements are observed in the shell of Sb\(_2\)Se\(_3\)/In\(_2\)S\(_3\), heterojunction nanorod (Figure S3, Supporting Information). A line scan (Figure 3f) further supported this claim. Both shoulders of In, Cd, and S could be observed in the line, corresponding to the In\(_2\)S\(_3\)-CdS nanocomposite shell. The element distribution mapping and EDX line scan results confirm that the Sb\(_2\)Se\(_3\) nanorod and In\(_2\)S\(_3\)-CdS composite buffer layer core/shell NRAs are successfully constructed on the surface via hydrothermal and following CBD method.

X-ray photoelectron spectroscopy (XPS) characterization was performed to check the chemical states of the Sb\(_2\)Se\(_3\) NRAs coated with different buffers (In\(_2\)S\(_3\), In\(_2\)S\(_3\)-CdS composites, and CdS). Curve fitting was further performed to determine the surface composition and chemical state of Cd, In, and S with different deposition process, as shown in Figure 4a. In S 2p spectra, the peaks at 161.5 and 162.7 eV, which corresponds to S 2p\(_{1/2}\) and S 2p\(_{3/2}\), respectively, were detected from all the samples. In the Cd 3d core level XPS spectra, the peaks at 405.2 and 411.9 eV, corresponding to Cd 3d\(_{3/2}\) and Cd 3d\(_{5/2}\) of CdS, respectively, were detected from all the samples but the NRAs with only In\(_2\)S\(_3\) coating. In the In 3d spectra, the peaks associating with In 3d\(_{3/2}\) and In 3d\(_{5/2}\) of In\(_2\)S\(_3\), were detected from the In\(_2\)S\(_3\), C5, C7, and C9 samples. The peak intensity decreases with the increase of...
Figure 4. Surface chemical analysis. a) XPS peak of Cd 3d, In 3d, and S 2p, respectively, obtained from the surface of Sb$_2$Se$_3$ NRAs coated with CdS, In$_2$S$_3$-CdS composites, and In$_2$S$_3$ buffer layers. b) The composition element ratios of the buffer layers. c) The optical transmittance spectra, and d) Tauc plots of the different buffer layers. e–j) Surface UPS spectra of these buffer layers, e) In$_2$S$_3$, f) C5, g) C7, h) C9, i) C11, and j) CdS.
deposition of CBD CdS layer, suggesting that the growth of CdS not only between the space of In$_2$S$_3$ flakes but also covered on flake surface. Moreover, no obvious peaks corresponding to In 3d are observed for the C11 sample, hinting that the good coverage of CdS layer on the In$_2$S$_3$ nanoflake films.

The UV–vis and ultraviolet photodetector spectroscopy (UPS) was employed to reveal the band structure of the composite buffer layers. Figure 4c shows the optical transmittance spectra of the layers. The corresponding effective bandgaps ($E_g$) can be obtained based on the Tauc equation, and the calculated results are shown in Figure 4d. The $E_g$ is 2.77, 2.72, 2.44, 2.35, 2.33, and 2.39 eV for single In$_2$S$_3$ nanoflake film, C5, C7, C9, C11, and single CdS film, respectively. At first, we characterize the surface energy level of the films. The Fermi level, valence band maximum (VBM) of the sample surfaces were obtained by fitting the cut-off binding energy and long-tails of the UPS spectra (Figure 4e–j). The conduction band maximum (CBM) was determined from the $E_g$ (Figure 4d) and VBM position. The CBM level is 3.74, 3.94, 4.28, 4.08, 4.18, and 4.30 eV for the single In$_2$S$_3$ nanoflake film, C5, C7, C9, C11, and single CdS film, respectively. Compared to the CdS layer, a slightly upshift of the CBM is observed for the In$_2$S$_3$-CdS composite layers. It suggests that the band structure (bandgap, CBM, VBM) of the combination of In$_2$S$_3$ and CdS is affected by the element-content and therefore depend on the CdS deposition time as the In$_2$S$_3$ layer has the same deposition condition for each sample.

In fact, the In$_2$S$_3$-CdS composite films (C5, C7, C9, or C11) is not stacked layer by layer, which more likely to be a mixture of In$_2$S$_3$ and CdS. The Sb$_2$Se$_3$ nanorod is first capped by In$_2$S$_3$ nanoflake films with a poor coverage due to the its ion-by-ion growth mechanism. Then, the following CdS layer caped both In$_2$S$_3$ nanoflake and the rest of Sb$_2$Se$_3$ nanorod surface to form a mixed buffer layer. As the CdS deposition time was longer than 9 min, the properties of CdS is dominant and the properties of In$_2$S$_3$-CdS composite buffers vary slightly with the CdS thickness. The surface CBM of the In$_2$S$_3$-CdS composite could be tuned by regulating the deposition time of CBD-CdS. It shows a trend of first decreasing, then increasing and then reducing with decreasing the CdS deposition time, suggesting that the interface between In$_2$S$_3$-CdS composite buffers and Sb$_2$Se$_3$ absorber has a tendency for a spike-like conduction band offset (CBO).

Due to the special structure of In$_2$S$_3$ nanoflake and CdS nanocomposites, we further characterize in detail the in-depth composition and band structures of the In$_2$S$_3$-CdS composite layer (C7) by performing the in-depth XPS and UPS measurement. Figure 5a illustrates the XPS depth profiling spectra of C7. Spectra of the binding energy of In 3d, Cd 3d, and S 2p core levels are presented. On the sample surface, Cd and S are clearly detected in the first few nanometers of the C7 sample surface as shown in the Cd 3d and S 2p spectra, whereas no obvious In is detected. After etching for 125 s (the reference etching rate is 0.60 nm s$^{-1}$ for Ta$_2$O$_5$), In is clearly detected at the near-surface region, and Cd and S peaks remain nearly unchanged, indicating that copresence of In$_2$S$_3$ and CdS in the near-surface region. The In, Cd, and S peaks keep nearly the same intensity as the etching time increases to 375 s. Furthermore, the In and Cd peaks decrease, and the S peak even disappears once the etching time increase to 500 s. This hints that the rear surface of C7 was reached for the etching time between 375 and 500 s. In the following UPS depth profile analysis, the spectra of the C7 sample with etching for 375 s could reveal the band structure of C7 rear surface. The corresponding UPS cutoff spectra of C7 for different etching time (125, 250, and 375 s) are shown in Figure 5b–d, respectively. As expected, the band structure shows an in-depth nonuniform behavior. The calculated VBMs and work functions are 1.48 and 16.24 eV for C7 with 125 s etching, 1.39 and 16.21 eV for 250 s, and 1.22 and 16.19 eV for 375 s, respectively. Thus, the CBM values are 4.02, 3.96, and 3.81 eV for C7 with etching time of 125, 250, and 375 s, respectively. These measurement results suggest that the In$_2$S$_3$-CdS composites layer (C7) has a gradual CBM structure (4.28 eV for the surface and 3.81 eV for the rear surface). The CBM of rear surface of C7 layer is slightly higher than that of the Sb$_2$Se$_3$ absorber (3.90 eV, Figure S4, Supporting Information).

To clarify the relationship between the different types of buffer layers and the photovoltaic properties of the Sb$_2$Se$_3$ solar cells, we fabricated the Sb$_2$Se$_3$ solar cells in a typical substrate configuration of Mo/MoSe$_2$/Sb$_2$Se$_3$/buffer (CdS, In$_2$S$_3$-CdS, In$_2$S$_3$/ZnO/Al-doped ZnO. Figure 6a–d and Table 1 show the statistic device parameters with different buffers. The typical CdS single buffer-based Sb$_2$Se$_3$ solar cell exhibits an open-circuit voltage ($V_{OC}$) of 405 mV, a short-circuit current density ($J_{SC}$) of 23.2 mA cm$^{-2}$, a fill factor (FF) of 63.60%, and a power conversion efficiency (PCE) of 7.15%. Meanwhile, the typical In$_2$S$_3$ single buffer-based cell shows a PCE of 3.41% from the declining $V_{OC}$, $J_{SC}$, and FF. Notably, it is clear that all devices with In$_2$S$_3$-CdS composite buffers (C5, C7, C9, and C11) demonstrate remarkable enhancement in $V_{OC}$, $J_{SC}$, and also PCE than the devices with CdS or In$_2$S$_3$ single buffer. The highest PCE of 9.19% is achieved for device with C7 buffer with $V_{OC}$ of 461 mV, $J_{SC}$ of 29.92 mA cm$^{-2}$, and FF of 66.67%. It is worth noting that $V_{OC}$ was promoted from 405 to 461 mV after the application and optimization of In$_2$S$_3$-CdS composite buffers, which will be discussed later. On the other hand, the $J_{SC}$ of solar cells with composite buffers exhibit slightly higher values than the device with CdS single buffer, and much higher than the device with single In$_2$S$_3$ buffer.

The external quantum efficiencies (EQEs) of champion cells from each group are displayed in Figure 6e. In the short wavelength range (350–600 nm), the EQE shows an obvious CdS

| Buffer | $V_{OC}$ [mV] | $J_{SC}$ [mA cm$^{-2}$] | FF [%] | PCE [%] |
|--------|---------------|-------------------------|--------|---------|
| In$_2$S$_3$ | 293 ± 15 | 22.1 ± 1.0 | 46.3 ± 3.4 | 3.01 ± 0.37 |
| C5 | 433 ± 12 | 26.50 ± 0.8 | 62.3 ± 1.1 | 7.15 ± 0.28 |
| C7 | 460 ± 6 | 28.9 ± 1.20 | 64.6 ± 2.6 | 8.55 ± 0.42 |
| C9 | 455 ± 3 | 28.9 ± 1.0 | 64.8 ± 1.9 | 8.38 ± 0.37 |
| C11 | 442 ± 8 | 28.0 ± 0.6 | 64.7 ± 2.0 | 8.00 ± 0.14 |
| CdS | 420 ± 14 | 26.9 ± 1.3 | 64.5 ± 1.7 | 7.32 ± 0.24 |
Figure 5. In-depth XPS and UPS analysis of In$_2$S$_3$-CdS composite layer (C7). a) In 3d, Cd 3d, and S 2p XPS spectra of the C7 with different etching time (0, 125, 250, 375, 500, and 600 s). b–d) UPS spectra of C7 at different depths during sputtering. b) 125 s, c) 250 s, and d) 375 s. e) Schematic diagram of band structures and carrier transport of the Sb$_2$Se$_3$ solar cell with an In$_2$S$_3$/CdS composite layer.

thickness-dependent behavior, where the EQE increase as the CdS deposition time decreases. The cell with In$_2$S$_3$ single buffer has a better photospectral response in this short-wavelength range. This could be attributed to its thinner thickness than the In$_2$S$_3$-CdS buffers and bigger bandgap than the CdS layer, which allow more photons pass through and be absorbed by the Sb$_2$Se$_3$. This could be ascribed to the narrow bandgap of CdS (2.39 eV) thin films, and the photons was absorbed by the CdS buffer before it arrived the Sb$_2$Se$_3$ layer without contribution much to the photocurrent due to its high doping density.[41] In the medium wavelength range (500–750 nm), the EQE was determined the Sb$_2$Se$_3$ absorber and absorber/buffer heterojunction interface quality. In comparison with CdS/Sb$_2$Se$_3$ interface, the coverage for In$_2$S$_3$ nanosheet on the Sb$_2$Se$_3$ rod surface is poor. The exposed Sb$_2$Se$_3$ surface is covered by the following CdS, and the coverage is improved after the formation of In$_2$S$_3$-CdS composite buffers. Hence, devices with composite buffers (C7, C9, C11) exhibit higher values than the reference CdS device, suggesting the variation in the heterojunction. In the longer wavelength range (750–1000 nm), the EQE values for devices with composite buffers show slight decrease. It could be ascribed to the incomplete collection of photogenerated carriers in the absorber, and the biased EQE measurement at −0.5 V (Figure S6, Supporting Information) show enhanced values in the longer wavelength range.

$J_{SC}$-decay and $V_{OC}$-decay were conducted to explore the photogenerated carrier dynamics in the solar cells.[29,42] The charge transport lifetime ($\tau_t$) could be derived from the $J_{SC}$-decay curves, while the $V_{OC}$-decay curves are corrected to the carrier recombination rates under the open-circuit conditions in the full solar cells. Figure 6g demonstrates the $V_{OC}$-decay curves of the Sb$_2$Se$_3$ nanorod solar cells with various buffers. The curves for the composite buffer-based solar cells exhibit much slower decays, in comparison with the reference CdS buffer-based device. The charge recombination lifetime ($\tau_r$) derived from the $V_{OC}$-decay curves was calculated to be 6.79 and 1.63 ms for C7 and
CdS device, respectively. This suggested that the carrier recombination was dramatically prohibited by involving the In$_2$S$_3$-CdS composite buffer in the device.

Temperature-dependent current density voltage ($J$–$V$–$T$) measurement was further carried out to investigate the mechanism of carrier transport at the heterojunction interface, as shown in Figure 6h. The activation energy of the main recombination paths can be obtained from the $V_{OC}$ versus temperature plot, and the relationship can be described by the following equation:

$$V_{OC} = E_a/q - A kT/q ln (J_{00}/J_0)$$

(1)

Where $E_a$ is a recombination activation energy, and the $J_{00}$ is a prefactor dependent on recombination paths, $A$ is an ideality factor, and $k$ is Boltzmann constant. According to the equation, $E_a$ can be obtained by the linear extrapolation of high temperature $V_{OC}$ data to $0 \text{ K}$, where $A$ and $J_{00}$ are not significantly temperature dependent. $E_a$ should equal the bandgap energy of Sb$_2$Se$_3$ absorber in the case of the bulk recombination, whereas it is lower than the bandgap in case of interface recombination. As shown in Figure 6h, the $E_a$ of Sb$_2$Se$_3$ solar cells with CdS single buffer was only 0.804 eV, much smaller that the bandgap of Sb$_2$Se$_3$ nanorod array solar cells. Morphological and structural analyses revealed that In$_2$S$_3$-CdS composite shell compactly covers the surface of Sb$_2$Se$_3$ nanorod. The best-performing device based on In$_2$S$_3$-CdS composite buffer achieved a PCE of 9.19% ($V_{OC}$ 461 mV), compared to that of the single In$_2$S$_3$ nanoflake buffer-based device of 3.41% (302 mV) and single CdS buffer-based device of 7.39% (405 mV). The gradient band structure, high-transmittance at short wavelengths, and low recombination of photogenerated carriers at the Sb$_2$Se$_3$/buffer nanorod array junction interfaces are responsible for the enhanced efficiency.

3. Conclusions

In conclusion, a low-temperature solution-processable In$_2$S$_3$ nanoflake/CdS composite layer is an efficient buffer layer for the Sb$_2$Se$_3$ nanorod array solar cells. Moreover, if the CBO becomes too large, the photogenerated electrons transferring from the Sb$_2$Se$_3$ absorber toward the top TCO contact are blocked by the high electron barrier at the junction interface, resulting in a decrease in photoreponse.

4. Experimental Section

Preparation of In$_2$S$_3$-CdS Nanocomposite Films: The In$_2$S$_3$ nanoflake film was grown using thioacetamide (C$_2$H$_5$NS, 99%, MACKLIN) and indium chloride (InCl$_3$, 99.999%, MACKLIN) as S and In precursors, respectively. In a typical procedure, 1.26 g citric acid (C$_6$H$_8$O$_7$, AR, 99.5%, MACKLIN) and 0.45 g C$_2$H$_5$NS were added into 60 mL of 25% ammonia (28%) to 585 mL of deionized water, stirring in a water bath at 70 °C for different time (5, 7, 9, 11, and 13 min), and the samples were washed with DI water and dried with clean dry air.
Fabrication of Sb$_2$Se$_3$ Nanorod Array Solar Cells: Sb$_2$Se$_3$ nanorod array solar cells were fabricated in a substrate configuration (glass/Mo/MoSe$_2$/Sb$_2$Se$_3$/buffer layer/i-ZnO/AZO), as described in our previous work.$^{[25]}$ The Mo back contact layer was prepared by 1200 W DC sputtering under a 0.3 Pa argon, in which the obtained Mo thickness was about 800 nm. Then, the as deposited W layer was transferred into a vacuum chamber for selenization. During the selenization, the vacuum chamber pressure was pumped down to $10^{-4}$ Pa and the substrate temperature was kept at 620 °C for 30 min. Approximately 1 μm thick Sb$_2$Se$_3$ nanorod array absorber layers were deposited by close space sublimation by a process of our previous recipe.$^{[25]}$ The deposition started when the pressure was below $10^{-2}$ Pa. First, the source and sample holder were warmed up to 480 and 270 °C, respectively, in 200 s, and maintained at the high temperatures for 100 s to obtain the Sb$_2$Se$_3$ absorbers with thickness of 1 μm. Differen buffers (In$_2$S$_3$ buffer, In$_2$S$_3$/CdS composite buffers, and CdS buffer) were prepared by the above process. Window layers of i-ZnO and AZO were deposited by RF magnetron sputtering to a thickness of 70 and 300 nm, respectively.

Characterization and Measurement: The morphology of the films was observed by high resolution field emission SEM (FEI nova nano SEM450) and atomic force microscopy (Veeco Multimode 8). XPS and UPS measurements were carried out using an X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Scientific), respectively. The measurements were repeated three times to ensure the reliability of the results. XPS and UPS measurements were performed on the devices using an AM1.5 solar simulator (ZAHNER GIMPS, Germany).

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:
Research data are not shared.

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