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Theoretical Insight into High-Efficiency Triple-Junction Tandem Solar Cells via the Band Engineering of Antimony Chalcogenides

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Antimony chalcogenides have become a family of promising photoelectric materials for high-efficiency solar cells. To date, single-junction solar cells based on individual antimony selenide or sulfide are dominant and show limited photoelectric conversion efficiency. Therefore, great gaps remain for the multiple junction solar cells. Herein, triple-junction antimony chalcogenides-based solar cells are designed and optimized with a theoretical efficiency of 32.98% through band engineering strategies with Sb₂S₃/Sb₂(S_{0.7}Se_{0.3})₃/Sb₂Se₃ stacking. The optimum Se content of the mid-cell should be maintained low, i.e., 30% for achieving a low defect density in an absorber layer. Therefore, Sb₂(S_{0.7}Se_{0.3})₃-based mid solar cells have contributed to elevate the external quantum efficiency in triple-junction devices by the full utilization of the solar spectrum. In a single-junction solar cell, the bandgap gradient is regulated through the Se content gradient along the depth profile of $Sb_2(S_{1-x}Se_x)_3$. Besides, an increasing Se content profile provides an additional built-in electric field for boosting hole charge carrier collection. Thus, the high charge carrier generation rate leads to a 17.96% improvement in the conversion efficiency compared with a conventional cell. This work may pave the way to boost the conversion efficiency of antimony chalcogenides-based solar cells to their theoretical limits.

1. Introduction

The growing demand for renewable and sustainable energy requires the development of cost-effective, stable, and efficient solar cells.^[1,2] Consequently, a diverse range of photoactive materials, such as CdTe,^[3,4] $Cu(In_{1-x}Ga_x)Se_2$,^[5,6] $Sb_2(S_{1-x}Se_x)_3$,^[7-9] and organic-inorganic hybrid perovskites,[10-13] have been used as solar cell materials, which have achieved impressive power conversion efficiencies (PCEs). $Sb_2(S_{1-x}Se_x)_3$ exhibits advantages, such as a high absorption coefficient, suitable bandgap, abundant raw materials, low toxicity, and easy processability.^[14-16] Recently, the certified PCE of the $Sb_2(S_{1-x}Se_x)_3$ solar cells reached 10%, which highlights the potential of $Sb_2(S_{1-x}Se_x)_3$ as one of the candidates for next-generation photovoltaic materials.^[17]

The bandgap of the $Sb_2(S_{1-x}Se_x)_3$ photoactive layer can be adjusted continuously by changing the ratio of the Se content (*x*),

because the crystal structures of Sb_2S_3 and Sb_2Se_3 are isomorphic. $^{[18-29]}$ Vacuum and non-vacuum methods have been

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successfully used to prepare Sb₂(S_{1-x}Se_x)₃ thin films. The vacuum method generally utilizes a thermal evaporation process. In 2016, Yang et al. prepared Sb₂(S_{1-x}Se_x)₃ thin films from Sb₂Se₃ and S powders of different contents as evaporation sources. As a result of changing the mass of S powder, they obtained an Sb₂(S_{1-x}Se_x)₃ solar cell with a PCE of 5.79% at a Se content of 80%.^[30] In 2018, Jaramillo-Quintero et al. prepared an Sb₂(S_{0.47}Se_{0.53})₃ solar cell with a PCE of 5.47% using Sb₂S₃ and Sb₂Se₃ of the same mass as that of the evaporation sources.^[31] Then, in 2019, Lu et al. prepared an Sb₂(S_{1-x}Se_x)₃ solar cell with a PCE of 6.3% using an Sb₂(S_{0.5}Se_{0.5})₃ powder as the evaporation source.^[32] Indeed, vacuum techniques have boosted the thin-film quality as well as the device performances of solar cells.^[33-66]

Meanwhile, non-vacuum methods, such as the solution process, can also be used to fabricate the Sb₂(S_{1-x}Se_x)₃ thin films. In 2018, Chen's group prepared the Sb₂(S_{1-x}Se_x)₃ thin films by spin-coating an Sb–S–Se precursor solution, which was followed by annealing. An Sb_{1.9}S_{2.2}Se_{0.9} solar cell with a PCE of 5.8% was fabricated by controlling the ratios of S and Se in the precursor solution.^[37] In 2020, their group used KSbC₄H₄O₇, Na₂S₂O₃, and SeC(NH₂)₂ as precursor materials to fabricate the Sb₂(S_{1-x}Se_x)₃ thin films with the Se contents of 0%, 17%, 29%, and 48% using the hydrothermal method. An optimal PCE of 10.0% was achieved when the Se content was 29%. An Sb₄Se₆ nanoribbon-based solar cells have been reported with an efficiency of 3.2%.^[38]

Meanwhile, the Sb₂(S_{1-x}Se_x)₃ solar cells, with a gradient bandgap, can be realized by adjusting the ratio of S and Se during their preparation or by post-processing the film.^[39–41] In 2018, Wang et al. prepared the Sb₂(S_{1-x}Se_x)₃ thin films with a gradient bandgap using the hydrothermal method followed by post-selenization. They demonstrated that the gradient bandgap could form an electrical field that could facilitate hole transport, thereby leading to an improved PCE of 6.14%.^[42] However, the mechanism of the gradient bandgap needs to be understood further due to its complex structure.^[43,44]

Meanwhile, the multijunction technology could improve the solar cell performance by facilitating the efficient use of spectral energy. This allows the device to exceed the Shockly–Queisser efficiency limit of the single-junction solar cell. This technology has already been widely used in various types of thin-film solar

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cells, such as thin-film silicon,^[45,46] organic,^[47] and perovskite solar cells.^[48] In thin-film silicon triple-junction tandem solar cells, the most optimal match between the amorphous silicon (a-Si:H) top-cell and microcrystalline silicon (µc-Si:H) bottom-cell (bot-cell) has been obtained by changing the Ge content of the amorphous silicon germanium (a-SiGe:H) middle-cell (mid-cell) to adjust the bandgap. The champion efficiency of the thin-film silicon solar cell has been achieved using an a-Si:H/a-SiGe:H/µc-Si:H triple-junction structure.^[49] The Sb₂(S_{1-x}Se_x)₃ has the same ability to adjust the bandgap as the a-SiGe:H. Similarly, Sb₂(S_{1-x}Se_x)₃ can also adjust the bandgap; therefore, it can also be used as a mid-cell in the Sb-based triple-junction thin-film solar cells.

Herein, a theoretical study of the Sb₂(S_{1-x}Se_x)₃ solar cells with an n-i-p planar heterojunction structure was conducted. First, models of the Sb₂(S_{1-x}Se_x)₃ solar cells at different Se contents were established to explore the influence of the Se content on the device performance. Subsequently, two kinds of bandgap gradient structures, with increasing and decreasing Se content profiles, were established, and their influence on the carrier transport in the device was explored. Finally, we introduced and investigated a novel Sb-based triple-junction tandem solar cell with an Sb₂(S_{1-x}Se_x)₃ mid-cell. A theoretical PCE of 32.98% was achieved. These results demonstrate the potential of Sb₂(S_{1-x}Se_x)₃ as an effective absorber in solar cells.

2. Results and Discussion

2.1. Bandgap Engineering of Sb₂(S_{1-x}Se_x)₃

Scheme 1a demonstrates the structural diagram of antimony chalcogenide solar cells, in which the Sb₂S₃ solar cell, the Sb₂(S_{1-*x*}Se_{*x*})₃ solar cell, and the Sb₂Se₃ solar cell are exhibited in detail. According to the first-principles calculation, Huang et al. found that the conduction band (E_c) of Sb₂(S_{1-*x*}Se_{*x*})₃ is mainly the bonding state of anion-p and Sb-p orbitals. With increasing the Se content, the E_c will downshift due to the stronger hybridization of Se-4p and Sb-5p, resulting in the bandgap reduction.^[50] Several calculated and experimental

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Scheme 1. a) Schematic diagram of antimony chalcogenide solar cells. b) Energy level position of antimony chalcogenide materials. c) Spectral absorption range of antimony chalcogenide materials.

studies have confirmed this tunable bandgap characteristic of $Sb_2(S_{1-x}Se_x)_3$, as listed in Table S2, Supporting Information.

Therefore, in the process of modeling the antimony chalcogenide photoactive layer, the E_c values of the Sb₂S₃ and Sb₂Se₃ were set as the -3.7 and -4.04 eV, respectively, which determined by the studies of Islam and Thakur and Li et al.^[51,52] Moreover, Wang et al. reported that the bandgap of Sb₂(S_{1-x}Se_x)₃ approximately decreases linearly with the increase in the Se content.^[15] Consequently, we established the energy band of the Sb₂(S_{1-x}Se_x)₃, in which E_c downshifts linearly from -3.7 to -4.04 eV with the increase in the Se content, which is shown in Scheme 1b.

Scheme 1c shows the corresponding spectral absorption range of antimony chalcogenide materials. It is demonstrated that the antimony chalcogenide materials could effectively absorb the energy photons in the visible and near-infrared regions, which are particularly suitable for the photoactive layers of thin-film solar cells. By adjusting the bandgap, the Sb₂(S_{1-x}Se_x)₃ photoactive layer can not only get the continuous change of spectral absorption limit, but also affect the built-in potential of the device. Therefore, it can be predicted that the tunable bandgap will affect short-circuit current density (J_{sc}) and the open-circuit voltage (V_{oc}) simultaneously and, thus, change the device performances.

2.2. $Sb_2(S_{1-x}Se_x)_3$ Solar Cells with Different Se Contents

Figure 1a shows a schematic diagram of the Sb₂(S_{1-x}Se_x)₃ solar cell. By maintaining the thickness of the Sb₂(S_{1-x}Se_x)₃ layer at 500 nm, models of Sb₂(S_{1-x}Se_x)₃ solar cells at different Se contents were developed. The specific device parameters of each layer, such as thickness, defect state, and doping concentration of Sb₂(S_{1-x}Se_x)₃ solar cells, are listed in Table S1 and S4, Supporting Information. Figure 1b–f shows the device

parameters of the $Sb_2(S_{1-x}Se_x)_3$ solar cells at different Se contents.

As the Se content of the Sb₂($S_{1-x}Se_x$)₃ solar cells gradually increased from 0% to 100%, the value of V_{oc} decreased from 1.21 to 0.74 V; meanwhile, the value of J_{sc} increased from 14.28 to 24.02 mA cm⁻². According to Figure 1f, the device absorption limit increased from 750 to 1050 nm, as the Se content increased. Therefore, the enhancement of the near-infrared response primarily improved J_{sc} . The variations in the V_{oc} and J_{sc} values were mostly due to the change in the Sb₂($S_{1-x}Se_x$)₃ bandgap, which resulted in an initial increase in the device performance of the Sb₂($S_{1-x}Se_x$)₃ solar cells; however, it then decreased.^[53] Consequently, the Sb₂($S_{1-x}Se_x$)₃ solar cells could maintain a high device performance of \approx 13.1% when the Se content was between 40% and 60%.

We linearly varied the bandgap of $Sb_2(S_{1-x}Se_x)_3$ with the Se content during the modeling process to reduce the complexity of the device models. However, small nonlinear characteristics between the bandgap and the Se content might be detected during the experiment, which may lead to a specific deviation of the Se content corresponding to the optimal PCE.^[54] As the change in the device performance with the Se content is similar, our simulation results are still informative for performing $Sb_2(S_{1-x}Se_x)_3$ solar cell experiments.

2.3. $Sb_2(S_{1-x}Se_x)_3$ Solar Cells with Different Gradient Bandgap Structures

Herein, $Sb_2(S_{1-x}Se_x)_3$ solar cells with increasing and decreasing Se content profiles were modeled. A similar solar cell with a constant Se content profile (50% Se content) was also introduced for comparison. Figure 2a–c shows the schematic diagrams of the structures.

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Figure 1. a) Bandgap, b) V_{oc} , c) J_{sc} , d) FF, e) PCE, and f) EQE curves of the $Sb_2(S_{1-x}Se_x)_3$ solar cells with various Se contents.

Figure 2d shows the distribution of the carrier generation rate of the $Sb_2(S_{1-x}Se_x)_3$ solar cells with different Se content gradient profiles. First, the light with different wavelengths was simultaneously incident from the electron transport layer (ETL) to the $Sb_2(S_{1-x}Se_x)_3$ layer. Herein, the short-wavelength light was initially completely absorbed because of its higher absorption coefficient. Then, the absorption capacity of the $Sb_2(S_{1-x}Se_x)_3$ layer gradually decreased with the increasing wavelength of light. Therefore, the carrier generation rate of the $Sb_2(S_{1-x}Se_x)_3$ solar cells progressively decreased with increasing depth. For the $Sb_2(S_{1-x}Se_x)_3$ solar cell with a decreasing Se content profile, the $Sb_2(S_{1-x}Se_x)_3$ layer near the ETL exhibited the highest rate of light generation owing to its narrowest bandgap and widest absorption spectral range. However, as the depth increased, the Se content of the $Sb_2(S_{1-x}Se_x)_3$ gradually decreased; accordingly, the light absorption capacity decreased. Therefore, the carrier generation rate of the $Sb_2(S_{1-x}Se_x)_3$ solar cell with a decreasing Se content reduced more rapidly with increasing depth, as compared with that of the $Sb_2(S_{1-x}Se_x)_3$ solar cell with a constant Se content profile. In contrast, for the $Sb_2(S_{1-x}Se_x)_3$ solar cell with an increasing Se content profile, the $Sb_2(S_xSe_{1-x})_3$ layer near the ETL exhibited the lowest rate of light generation owing to its widest bandgap and narrowest absorption spectral range. The Se content of the $Sb_2(S_{1-x}Se_x)_3$ layer gradually increased with increasing depth; hence, its light absorption capacity continuously improved. Consequently, the most uniform carrier generation rate distribution was obtained.

Figure 2e,f shows the electron and hole concentration distributions of the $Sb_2(S_{1-x}Se_x)_3$ solar cells at different Se content gradient profiles. The first 120 nm of the $Sb_2(S_{1-x}Se_x)_3$ layer shows that the $Sb_2(S_{1-x}Se_x)_3$ solar cell with a decreasing Se content profile exhibited higher carrier concentrations than those

obtained with a constant Se content profile: this is because of the larger rate of carrier generation in this region. Meanwhile, the increased ratio of hole concentration was higher than that of the electron concentration. This is because the decreasing Se content profile could form a widening bandgap structure, which led to the formation of an additional electric field that accelerated electron migration and decelerated hole migration (Figure 2c).^[55] Furthermore, the additional electric field allows the electrons generated in this area to reach the interface quicker and be collected by the ETL. However, it was demonstrated that the hole mobility of $Sb_2(S_{1-x}Se_x)_3$ is inherently deficient. Nevertheless, the hole transport could be further limited by the additional electric field after decreasing the Se content profile, which resulted in the severe accumulation of holes. In contrast, the $Sb_2(S_{1-x}Se_x)_3$ solar cell with an increasing Se content profile exhibited the most uniform carrier concentration.

Figure 2g shows the carrier recombination rate distributions of the $Sb_2(S_{1-x}Se_x)_3$ solar cells at different Se content gradient profiles. The majority of the photogenerated carriers of the $Sb_2(S_{1-x}Se_x)_3$ solar cells with decreasing Se content profiles were generated on the side close to the ETL. They were also blocked by an additional electric field, which resulted in the majority of the holes being unable to reach the hole transport layer (HTL). Therefore, the device suffered from serious carrier recombination. However, the photogenerated carriers were distributed more uniformly in the $Sb_2(S_{1-x}Se_x)_3$ layer of the $Sb_2(S_{1-x}Se_x)_3$ solar cell with an increasing Se content. Furthermore, the additional electric field promoted hole migration, but impeded electron migration. The increasing Se content profiles could balance the charge carrier transport and effectively inhibit the recombination in the $Sb_2(S_{1-x}Se_x)_3$ solar cells, because the electron mobility was higher than the hole mobility.

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Figure 2. Schematic diagram of the $Sb_2(S_{1-x}Se_x)_3$ solar cell with a) a constant Se content profile, b) an increasing Se content profile, and c) a decreasing Se content profile. d) Carrier generation rate distribution, e) free electrons concentration distribution, f) holes concentration distribution, and g) carrier recombination rate distribution of the $Sb_2(S_{1-x}Se_x)_3$ layers with different Se content gradient profiles. h) *J*–*V* curves and i) EQE curves of the $Sb_2(S_{1-x}Se_x)_3$ solar cells with different Se content gradient profiles.

Figure 2h shows the J-V curves of the Sb₂(S_{1-x}Se_x)₃ solar cells with different Se content gradient profiles. The specific performance parameters are summarized in Table S5, Supporting Information. The $Sb_2(S_{1-x}Se_x)_3$ solar cell with a constant Se content profile was observed to yield a $V_{\rm oc}$ of 0.98 V, a $J_{\rm sc}$ of 19.77 mA cm^{-2} , a fill factor (FF) of 67.94%, and a PCE of 13.14%. In comparison, the values of $J_{\rm sc}$ and FF of the $Sb_2(S_{1-x}Se_x)_3$ solar cells with a decreasing Se content were 3.96 mA cm^{-2} and 36.55%, respectively. As shown in Figure 2i, the maximum spectral response of the $Sb_2(S_{1-r}Se_r)_3$ solar cells was as low as 30%, which indicates that severe carrier recombination occurred. This resulted in the lowest PCE of 1.33%. However, the J_{sc} and FF values of the Sb₂(S_{1-x}Se_x)₃ solar cells with an increasing Se content increased significantly to 24.43 mA cm⁻² and 79.40%, respectively. Its external quantum efficiency (EQE) response improved over the entire spectral band, and its absorption limit widened to 1050 nm. Although $V_{\rm oc}$

of the device decreased to a certain degree, the device achieved the highest PCE of 15.50%.

Meanwhile, the device performance could be influenced by the simultaneous change in the absorption coefficient and bandgap with varying Se content gradient distributions. To study the effects of these two aspects separately, two types of device models were established. In model one, the bandgap was fixed to be the same as that of the $Sb_2(S_{0.5}Se_{0.5})_3$, and only a gradual distribution of the absorption coefficient was formed. In model two, the absorption coefficient was fixed to be the same as that of the $Sb_2(S_{0.5}Se_{0.5})_3$, and only a gradual distribution of the bandgap was formed.

In model one, only the carrier generation rate distribution changed when the absorption coefficient was modified. The characteristics of the $Sb_2(S_{1-x}Se_x)_3$ solar cells with a constant bandgap and gradient absorption coefficients are shown in **Figure 3**, whereas the specific performance parameters are listed







Figure 3. a) Carrier generation rate distribution, concentration distribution of free c) electrons and d) holes, and e) carrier recombination rate distribution in the $Sb_2(S_{1-x}Se_x)_3$ layer of the $Sb_2(S_{1-x}Se_x)_3$ layer of the $Sb_2(S_{1-x}Se_x)_3$ layer of the $Sb_2(S_{1-x}Se_x)_3$ solar cells with different Se content gradient profiles. For the $Sb_2(S_{1-x}Se_x)_3$ layer of the absorption coefficient changed with the regulation of the Se content, whereas the bandgap was the same as that of $Sb_2(S_{0.5}Se_{0.5})_3$.

in Table S6, Supporting Information. Due to the uneven distribution of the carrier generation rate, the $Sb_2(S_{1-x}Se_x)_3$ solar cell with a decreasing Se content profile had the highest carrier recombination rate, which resulted in a decrease in the FF value and a decrease in the spectral response from 580 to 710 nm. However, the long wave response of the $Sb_2(S_{1-x}Se_x)_3$ solar cells with an increasing Se content improved due to the presence of a narrow bandgap $Sb_2(S_{1-x}Se_x)_3$ with a Se content of more than 50%. Overall, the PCE of the $Sb_2(S_{1-x}Se_x)_3$ solar cell with a decreasing Se content was 12.80%, which was slightly lower than that of the $Sb_2(S_{1-x}Se_x)_3$ solar cell with a constant Se content profile (13.14%). In contrast, the $Sb_2(S_{1-x}Se_x)_3$ solar cell with an increasing Se content profile had the most uniform carrier generation rate distribution. This result could achieve the shortening of the distance needed for the holes to be collected by the HTL, thus reducing the recombination probability (Figure 3e). Consequently, the Jsc and FF values of the device increased to 21.82 mA cm⁻² and 69.47%, respectively, resulting in a higher PCE of 14.90%.

Meanwhile, in model two, changing the bandgap distribution alone introduced an additional electric field into the $Sb_2(S_{1-x}Se_x)_3$ layer. The characteristics of the $Sb_2(S_{1-x}Se_x)_3$ solar cells at constant absorption coefficients and gradient bandgap are shown in **Figure 4**, whereas the specific performance parameters are listed in Table S7, Supporting Information. Figure 4c,d shows that the additional electric field has a strong regulating effect on the carrier concentration distribution. Figure 4e shows the carrier recombination rate distribution of the $Sb_2(S_{1-x}Se_x)_3$ layers with different Se content gradient profiles. For the $Sb_2(S_{1-x}Se_x)_3$ solar cell with a decreasing Se content profile, the hole accumulation caused by an additional electric field resulted in an increase in the carrier recombination rate and a sharp decrease in the PCE. In contrast, the additional electric field improved the migration ability of holes in the Sb₂(S_{1-x}Se_x)₃ solar cell with an increasing Se content profile. This further balanced the transport of electrons and holes. Therefore, the device exhibited the best carrier transport characteristics; the J_{sc} , FF, and PCE values increased from 19.77 to 23.04 mA cm⁻², 67.94% to 79.17%, and 13.14% to 14.78%, respectively. However, the increasing Se content profile directly leads to a reduction in the V_{oc} value, which may be associated with the band structure variation.

In summary, the uniform distribution of the rate of carrier generation as well as the formation of an additional electric field of the Sb₂(S_{1-x}Se_x)₃ solar cell with an increasing Se content profile could improve the device performance by enhancing the values of J_{sc} and FF. Therefore, this device structure is promising for producing highly efficient single-junction Sb₂(S_{1-x}Se_x)₃ solar cells. Furthermore, our technology can also be applied to the device design of other photoactive layers properties of adjustable bandgap, i.e., $a/\mu c$ -Si_{1-x}Ge_x:H, Cu(In_{1-x}Ga_x)Se₂, In_xGa_{1-x}As, and perovskite (Table S3, Supporting Information).

2.4. Triple-Junction Tandem Solar Cell with an $Sb_2(S_{1-x}Se_x)_3$ Mid-Cell

 $Sb_2(S_{1-x}Se_x)_3$ is suitable for use as the mid-cell of an Sb-based triple-junction tandem solar cell owing to its tunable bandgap. The schematic diagram and energy band diagram of the







Figure 4. a) Carrier generation rate distribution, concentration distribution of free c) electrons and d) holes, and e) carrier recombination rate distribution in the $Sb_2(S_{1-x}Se_x)_3$ layer of the $Sb_2(S_{1-x}Se_x)_3$ layer of the $Sb_2(S_{1-x}Se_x)_3$ layer of the $Sb_2(S_{1-x}Se_x)_3$ solar cells with different Se content gradient profiles. For the $Sb_2(S_{1-x}Se_x)_3$ layer of thes devices, only the bandgap changed with the regulation of the Se content, whereas the absorption coefficient was the same as that of $Sb_2(S_{0.5}Se_{0.5})_3$.

triple-junction tandem solar cell are shown in **Figure 5**a and Figure S1, Supporting Information, respectively. The triplejunction tandem solar cells consist of fluorine-doped tin oxide (FTO)/TiO₂/Sb₂S₃/spiro-OMeTAD/TiO₂/Sb₂(S_{1-x}Se_x)₃/ spiro-OMeTAD/TiO₂/Sb₂Se₃/spiro-OMeTAD/Au. To fully absorb the sunlight, TiO₂/Sb₂S₃/spiro-OMeTAD, TiO₂/ Sb₂(S_{1-x}Se_x)₃/spiro-OMeTAD, and TiO₂/Sb₂Se₃/spiro-OMeTAD sub-cells are acted as the top-cell, middle-cell, and bottom-cell, respectively. The specific device parameters of each layer, such as thickness, defect state, and doping concentration of triplejunction tandem solar cells, are listed in Table S1 and S8, Supporting Information. We achieved a theoretical efficiency of 32.98% ($V_{oc} = 3.44 \text{ V}$, $J_{sc} = 11.08 \text{ mA cm}^{-2}$, and FF = 86.49%) using an Sb₂(S_{0.7}Se_{0.3})₃ mid-cell in the Sb-based triple-junction tandem solar cell. This was an improvement when compared with the efficiency of the Sb₂S₃/Sb₂Se₃ double-junction solar cell (PCE = 26.64%) that we modeled. This indicates that the application of the Sb₂(S_{1-x}Se_x)₃ solar cells as mid-cells results in the more efficient use of the spectral energy, reduction in heat loss, and further improvement in the PCE of the Sb-based solar cells.

According to the detailed balance theory, Vos demonstrated that the theoretical PCE of 49% could be achieved for a triplejunction tandem solar cell structure, which is higher than our



Figure 5. a) Schematic diagram of the $Sb_2S_3/Sb_2(S_{0.7}Se_{0.3})_3/Sb_2Se_3$ triple-junction tandem solar cells. The magenta layer represents an antimony chalcogenides photoactive layer. The gray layer represents an FTO substrate. The blue layer represents a TiO₂ ETL. The green layer represents a spiro-OMeTAD HTL. The golden layer represents an Au electrode. The antimony chalcogenides-based tandem solar cells are assembled by depositing each layer of the Sb_2S_3 top-cell, the $Sb_2(S_{1-x}Se_x)_3$ middle-cell, and the Sb_2Se_3 bottom-cell in sequence. Here, a spiro-OMeTAD/TiO₂ tunnel junction formed by the high-doped carrier layers is a reversed p/n junction that is electrically connecting two sub-cells. b) *J*–*V* curves and c) EQE curves of the $Sb_2S_3/Sb_2(S_{1-x}Se_x)_3/Sb_2Se_3$ triple-junction tandem solar cell. Here, the Se content (*x*) in the antimony chalcogenides equals 0.3.

simulated PCE.^[56–60] This is because Vos's simulation considers only the bandgap and does not consider other properties of the photovoltaic materials, nor the heterojunction structure of the sub-cell and the tunneling junction between the sub-cells. In contrast, our simulations are based on the actual device material properties and device structure, presenting the theoretical PCE that belongs to the antimony chalcogenides-based triple-junction tandem solar cells.

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Furthermore, using the similar simulation method, the theoretical PCEs of 30.4% and 31.79% were reported for triplejunction tandem solar cells based on different bandgap perovskite materials.^[61,62] It can be predicted that through continuous optimization, the PCEs of antimony chalcogenides and perovskite-based triple-junction tandem solar cells are expected to exceed 30%. In the pursuit of high-performance solar cells, theoretical modeling and simulation can help understand the mechanism of solar cell devices and find out the key factors affecting the device performance. Besides, one could decrease the time and materials cost for conventional trial and error mode. Eventually, it can play a prominent role in shortening the research and development cycle and reducing the devices.

The efficient performance of the Sb-based triple-junction tandem solar cell depends on its high-quality photoactive layers and suitable Se content in the Sb₂(S_{1-x}Se_x)₃ mid-cell. **Figure 6** shows a contour map of the triple-junction tandem solar cell performance when the Se content and defect densities are varied. As shown in Figure 6a, the triple-junction tandem solar cell had a V_{oc} of up to 3.42 V when the defect state and the Se content were 10¹⁴ cm⁻³ and 0%, respectively. However, the V_{oc} value decreased, as the defect state and the Se content increased. The increase in the Se content could reduce the bandgap of $Sb_2(S_{1-x}Se_x)_3$, thereby decreasing the V_{oc} value of the mid-cell. Meanwhile, the increase in the defect state could raise the carrier recombination, which reduces the performance of all the sub-cells. Therefore, the V_{oc} value of the triple-junction tandem solar cell was 2.25 V, when the Se content and the defect density were 100% and 10^{18} cm⁻³, respectively.

The variation in I_{sc} of the triple-junction tandem solar cell with different Se contents and defect densities is shown in Figure 6b. When the Se content of the mid-cell is low, an insufficient current density is generated; hence, the total current density of the triple-junction tandem solar cell is limited by the mid-cell. Therefore, increasing the Se content of the $Sb_2(S_{1-x}Se_x)_3$ midcell gradually increases its light absorption capacity, thereby causing I_{sc} of the triple-junction tandem solar cell to also increase. However, when the Se content of the $Sb_2(S_{1-x}Se_x)_3$ mid-cell was higher than 60%, $J_{\rm sc}$ of the triple-junction tandem solar cell was restricted by the Sb₂Se₃ bot-cell. Therefore, the total current of the triple-junction tandem solar cell is only slightly increased by further increasing the Se content of the mid-cell. Meanwhile, the suppression of the defect density could reduce the carrier recombination, thereby increasing the J_{sc} value. Consequently, the triple-junction tandem solar cell achieved the highest I_{sc} value of 10.70 mA cm^{-2} when the defect state and the Se content were 10^{14} cm⁻³ and 100%, respectively.

Figure 6c shows the variation in the FF of the triple-junction tandem solar cell with different Se contents and defect densities. The triple-junction tandem solar cell achieved a high FF when the Se content of the mid-cell was low due to the large current



Figure 6. Contour maps of the performance of the triple-junction tandem solar cells with varied $Sb_2(S_{1-x}Se_x)_3$ mid-cell Se contents and defect state of the whole cell. a) Open-circuit voltage V_{oc} . b) Short-circuit current density J_{sc} . c) FF. d) PCE.

difference between the sub-cells. However, the FF decreased with an increase in the Se content. The best FF of 84.30% was achieved when the defect density and the Se content were 10^{14} cm⁻³ and 0%, respectively.

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The variation in the device parameters determines the final performance of the triple-junction tandem solar cell. In general, $V_{\rm oc}$ and FF tend to decrease, whereas $J_{\rm sc}$ increases with an increase in the Se content of the $Sb_2(S_{1-x}Se_x)_3$ mid-cell. Table S9, Supporting Information, lists the best device performances of the triple-junction tandem solar cells at different defect densities. The device achieved the best PCE of 27.99% when the defect density and the Se content of the $Sb_2(S_{1-x}Se_x)_3$ mid-cell were 10^{14} cm⁻³ and 30%, respectively. Interestingly, the optimal Se content of the mid-cell increased with an increase in the defect state. This is mainly because J_{sc} of the triple-junction tandem solar cell at a higher defect density decreases more rapidly when the Se content is decreased, as shown in Figure S2, Supporting Information. As the defect state increased to 10¹⁸ cm⁻³, the triple-junction tandem solar cell achieved the best performance using an $Sb_2(S_{1-x}Se_x)_3$ mid-cell with 70% Se content; however, the PCE was 9.12%. It should be noted that the decrease in J_{sc} was the most severe when the defect state increased. This was also the main reason for the deterioration of the device performance.

The use of the $Sb_2(S_{1-x}Se_x)_3$ mid-cell with 30% Se content can result in the Sb-based triple-junction tandem solar cell achieving the highest device performance when it does not comprise a defect state. According to Figure 5b, the V_{oc} values of the Sb₂S₃ top-cell, Sb₂(S_{0.7}Se_{0.3})₃ mid-cell, and Sb₂S₃ bot-cell were 1.41, 1.21, and 0.84 V, respectively. The value of $V_{\rm oc}$ of the triple-junction tandem solar cell at 3.46 V was approximately equal to the sum of the value of $V_{\rm oc}$ of the three sub-cells at 3.44 V. Meanwhile, the J-V curves show that the values of J_{sc} of the three sub-cells were approximately equal, indicating that the solar spectral energy was evenly distributed among the three sub-cells. Consequently, the triple-junction tandem solar cell had a $J_{\rm sc}$ of 11.08 mA cm⁻². Furthermore, Figure 5c shows that the spectral energy with a wavelength less than 1050 nm is fully absorbed. Finally, the Sb-based triple-junction tandem solar cell achieved a theoretical efficiency of 32.98%.

It is worth noting that the triple-junction tandem solar cell obtains a high $V_{\rm oc}$ of 3.44 V. $V_{\rm oc}$ is given by the following expression^[63]

$$V_{\rm oc} = \frac{E_{\rm g}}{q} - \frac{nkT}{q} \ln\left(\frac{J_{00}}{J_{\rm ph}}\right) \tag{1}$$

where *k* is the Boltzmann constant, *T* is the temperature, *q* is the elementary charge, $J_{\rm ph}$ is the photogenerated current density, $E_{\rm g}$ is the bandgap, and J_{00} is the weakly temperature-dependent prefactor. The formula indicates that $V_{\rm oc}$ is directly related to $E_{\rm g}$ of the photoactive layer. The larger the bandgap, the higher the value of $V_{\rm oc}$. On the other hand, the difference between $E_{\rm g}/q$ and $V_{\rm oc}$ can be defined as the $V_{\rm oc}$ deficit. Chen and Tang demonstrates that the minimum $V_{\rm oc}$ deficit at room temperature is about 0.24–0.28 V when $E_{\rm g}$ ranges from 1.0 to 1.7 eV.^[64] Here, we assume that the $V_{\rm oc}$ deficits of Sb₂S₃, Sb₂(S_{0.7}Se_{0.3})₃, and Sb₂Se₃ solar cells are 0.28, 0.26, and 0.25 eV, respectively. Then, by subtracting the deficits from the sum of $E_{\rm g}/q$ with each sub-cell,

the ideal $V_{\rm oc}$ of triple-junction tandem solar cells can be predicted as 3.66 V, which is consistent with our simulation.

Furthermore, similar V_{oc} values have also been obtained in the simulations and experiments of other kinds of triple-junction tandem solar cells. McMeekin et al. established a FA_{0.83}Cs_{0.17}Pb(Br_{0.7}I_{0.3})₃ top-cell (1.94 eV)/MAPbI₃ mid-cell (1.57 eV)/FA_{0.6}MA_{0.4}Pb_{0.4}Sn_{0.6}I₃ bot-cell (1.34 eV) triplejunction tandem solar cell and obtained a $V_{\rm oc}$ of $3.30 \, {\rm V}^{[62]}$ Zhang et al. designed a FAPbIBr₂ top-cell (1.96 eV)/MAPbI₃ mid-cell (1.55 eV)/p-Si bot-cell (1.12 eV) triple-junction tandem solar cell and obtained a V_{oc} of 3.42 V.^[61] Besides, in the experimental preparation of high-cost and high-efficiency GaAs-based solar cells, Geisz et al. fabricated a Ga_{0.51}In_{0.49}P top-cell (1.83 eV)/In_{0.04}Ga_{0.96}As middle-cell (1.34 eV)/In₃₇Ga₆₃As bottom-cell (0.89 eV) triple-junction tandem solar cell and achieved a V_{oc} of 3.28 V.^[65] These results demonstrate the effectiveness of our methodology in constructing antimony chalcogenides-based triple-junction tandem solar cells.

To the best of our knowledge, there is no experimental report on the antimony chalcogenides-based triple-junction tandem solar cell. However, we can predict its performance based on the experimental results of the single-junction solar cells. The current research status for antimony chalcogenides-based single-junction solar cells is summarized in Figure S3, Supporting Information. The reported optimal V_{oc} values are 1.098 V for the Sb₂S₃ solar cell, 0.494 V for the Sb₂Se₃ solar cell, and 0.792 V for the $Sb_2(S_{1-x}Se_x)_3$ solar cell. If we combine these three single-junction cells, we can get a maximum V_{oc} of 2.384 V. On the other hand, according to the research status of I_{sc} summarized in Figure S3, Supporting Information, it can be found that the current densities of the Sb₂S₃ top-cell and the $Sb_2(S_{1-x}Se_x)_3$ mid-cell can match with that of the Sb_2Se_3 bot-cell. Therefore, the triple-junction tandem solar cell can get about 1/3 of the maximum J_{sc} of the Sb₂Se₃ solar cell, which is about 10.86 mA cm⁻². Finally, the FF of the triple-junction tandem solar cell is set to be consistent with that of the highest antimony chalcogenides-based single-junction solar cell, which is 70.3%.^[21] As a result, by multiplying the three predicted device parameters, we get a PCE of 18.2% for the triple-junction tandem solar cell, which lies in a certain distance from the theoretical PCE of 32.98%. Among them, $V_{\rm oc}$, $J_{\rm sc}$, and FF have 30.7%, 2.0%, and 18.7% rooms for improvement, respectively.

It can be seen that J_{sc} is very close to the theoretical level at present. However, the low V_{oc} becomes one of the main factors that limit the performance of triple-junction tandem solar cells, which should be considered as a priority in experimental optimization. The high V_{oc} deficit is mainly caused by the following aspects: 1) high interface recombination rate caused by the dangling bond or mismatching lattice; 2) high concentrations of deep defects in the antimony chalcogenide layers; and 3) large band tail states low crystallinity or microstructure disorder.^[20,66–69] Therefore, various optimization methods (i.e., adding high-quality buffer layers, effective doping strategies, highly ordered longitudinal growth of (Sb₄Se₆)_n ribbons, etc.) should be conducted to keep the V_{oc} deficit as low as possible.^[70–72]

Furthermore, the enhancement of V_{oc} indicates the suppression of reverse saturation current, which can effectively increase the parallel resistance of the device and improve the FF. Therefore, suitable optimization strategies are likely to boost

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 $V_{\rm oc}$ and FF of the device simultaneously, which could lengthen the short board of the devices and make the antimony chalcogenides-based single- and triple-junction tandem solar cells extremely competitive. With the advantages of abundant raw materials and simple preparation methods, their large-scale industrial production is expected to be realized in the future.

3. Conclusion

In summary, the 33% efficient triple-junction $Sb_2S_3/$ Sb₂(S_{0.7}Se_{0.3})₃/Sb₂Se₃ solar cells based on have been demonstrated by means of band regulating strategies. The enhanced optoelectronic conversion efficiency has been achieved by introducing Se content gradient in the absorber material, i.e., $Sb_2(S_{1-x}Se_x)_3$ device in the n-i-p triple-stacked solar cells. Besides, the EQE has been enhanced through the band alignment of three types of antimony chalcogenides-based absorber materials toward full utilization of solar spectrum. In addition, band alignment of the absorber material along its depth profile has promoted the hole transport. The $Sb_2(S_{1-x}Se_x)_3$ solar cell with an increased Se content adsorbs the incident light more efficiently. The breakthrough efficiency of triple-junction tandem solar cells has been guaranteed with the improvement of most device parameters, i.e., V_{oc} and FF compared with that of the Sb₂S₃/Sb₂Se₃ tandem solar cells.

This work highlights the possibilities of achieving efficiency enhancement when prepared with physical vapor deposition approaches. In addition, the generation and separation of charge carriers have been boosted with the gradient in the band alignment in the $Sb_2(S_{1-x}Se_x)_3$ thin film. Indeed, the Se content gradients have been achieved with Cu(In,Ga)Se₂ thin-film solar cells, which validates the design of $Sb_2S_3/Sb_2(S_{0.7}Se_{0.3})_3/Sb_2Se_3$ triple-junction tandem solar cells. Moreover, the general approach of band alignment could provide insight into the improvement of conversion efficiency of multiple junction solar cells.

4. Experimental Section

Device Performances: A simulation software called wx-AMPS was used in this study.^[73] The software algorithm uses the Newton method and Gummel method to solve the Poisson equation along with the electron and hole continuity equations under 1D conditions for the entire solar cell. Simulation results, such as photovoltaic parameters (V_{ocr} , J_{sc} , FF, and PCE), current density–voltage (*J*–V) curve, EQE spectra, energy band diagram, distribution of carrier concentration, generation rate, recombination rate, electric field, and current, can be obtained from the calculations, which facilitate the in-depth study of how different conditions affect the photovoltaic characteristics of the solar cell.^[74] The simulation was carried out under an AM 1.5G solar spectrum, with an incident power density of 100 mW cm⁻² at a temperature of 300 K.

Band Alignment Diagram and Device Fabrication: A transparent conducting film/ETL/Sb₂(S_{1-x}Se_x)₃ photoactive layer/HTL/back electrode Sb₂(S_{1-x}Se_x)₃ solar cell model structure was established in this study. We developed 101 models by changing the Se content from 0% to 100%, with the Se content of two adjacent models differing by 1%. The transparent conducting oxide, ETL, HTL, and back electrode were based on the material properties of the FTO, TiO₂, spiro-OMeTAD, and Au. The specific parameters of each layer are listed in Table S1, Supporting Information. The variation in the Se content could change the bandgap offset between the Sb₂(S_{1-x}Se_x)₃ layer and the carrier transport layers, thereby affecting the carrier transport and collection in the device. Therefore, E_c of the ETL and valence band (E_v) of the HTL were aligned with E_c and E_v of the Sb₂(S_{1-x}Se_x)₃ layers, respectively, by adjusting the affinity of the carrier transport layers. This eliminated the influence of the bandgap offset on the device performance.

Absorber Materials Optimization: The Sb₂(S_{1-x}Se_x)₃ absorber materials with increasing Se (Se content increasing continuously from 0% to 100%) and decreasing Se content profiles (Se content decreasing continuously from 100% to 0%) were produced. The difference in the Se content of the two adjacent Sb₂(S_{1-x}Se_x)₃ layers was 1%. Eventually, a triple-junction tandem solar cell with an Sb₂S₃/Sb₂(S_{1-x}Se_x)₃/Sb₂Se₃ structure was fabricated, with the Se content varying from 0% to 100%. The defect density of each photoactive layer was varied from 10¹⁴ to 10¹⁸ cm⁻³.

Optical Coupling between the Adjacent Solar Cells: In a triple-junction tandem structure, the Sb₂S₃ top-cell and the Sb₂Se₃ bot-cell are designed to absorb short and long wavelength photons of incident solar radiation, respectively. Eventually, the current matching of the triple-junction tandem solar cell can be obtained by flexible bandgap modulation of the Sb₂(S_{1-x}Se_x)₃ mid-cell (Figure S4, Supporting Information). Subsequently, the spectral responses are simulated with EQE (Figure S5, Supporting Information). The optical coupling between each sub-cell is realized by the transfer matrix method, which systematically considers the internal reflection and transmission between internal layers.^[75]

Electrical Connection in the Tandem Solar Cells: The antimony chalcogenides-based triple-junction tandem solar cells are fabricated in sequence. In brief, the Sb₂S₃ top-cell was first fabricated over FTO glass with the sequent deposition of TiO₂, Sb₂S₃, and spiro-OMeTAD films. Then, the Sb₂(S_{1-x}Se_x)₃ middle-cell was fabricated over top-cell, with deposition of TiO₂, Sb₂(S_{1-x}Se_x)₃, and spiro-OMeTAD films. Next, the Sb₂Se₃ bottom-cell was assembled with the thin-film stacking of TiO₂, Sb₂Se₃, and spiro-OMeTAD. Eventually, the whole tandem solar cell was formed by the Au thin films coating over the surface of spiro-OMeTAD. Here, a spiro-OMeTAD/TiO₂ tunnel junction formed by the high-doped carrier layers is a reversed p/n junction that is electrically connecting two subcells. The high-quality tunnel junctions we modeled have an ohmic contact with no rectifying behavior to allow the electrons and holes to recombine and form a continuous current flow, as shown in Figure S1, Supporting Information.

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.

Keywords

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