

Engineering microstructures for efficient $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ solar cells

Rongfeng Tang¹, Tao Chen^{1,†}, and Liming Ding^{2,†}

¹Hefei National Laboratory for Physical Sciences at Microscale, Key Laboratory of Materials for Energy Conversion (CAS), School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, China

²Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China

Citation: R F Tang, T Chen, and L M Ding, Engineering microstructures for efficient $\text{Sb}_2(\text{S}_x\text{Se}_{1-x})_3$ solar cells[J]. *J. Semicond.*, 2021, 42(7), 070203. <http://doi.org/10.1088/1674-4926/42/7/070203>

To realize solar-to-electrical energy conversion, several kinds of solar technologies have been developed since the invention of silicon solar cells. Recently, antimony selenosulfide $\text{Sb}_2(\text{S},\text{Se})_3$ (including Sb_2S_3 and Sb_2Se_3) has been considered one of the promising emerging materials for solar cell applications due to simple chemical composition, abundant elemental storage and excellent stability^[1]. In terms of practical applications, a solar technology should simultaneously possess high-efficiency, low-cost and long-term stability. The stability for these materials and related devices has already been examined^[2–4]. In particular, Sb_2Se_3 solar cells have passed through the stringent stability test^[4]. Furthermore, the compound is non-toxic and doesn't contain rare elements, which sets the ground for future low-cost production. The optical bandgap for antimony selenosulfide lies in 1.1–1.7 eV^[1], falling into the optimal region for sunlight absorption. According to the Shockley-Queisser limit, ~32% PCE can be expected for $\text{Sb}_2(\text{S},\text{Se})_3$ solar cells.

In practical, one of the basic requirements for making efficient solar cells is to prepare high-quality absorber films. Recently, Tang *et al.* reported a hydrothermal deposition method (Figs. 1(a) and 1(b)), which produced flat and compact $\text{Sb}_2(\text{S},\text{Se})_3$ films with large grains^[5]. The increase of selenium content in the compound can suppress the deep-level defects of anti-site Sb_s , while not yielding new defect Sb_{Se} . This characteristic suggests an effective strategy for suppressing the deep-level defects. At suitable $\text{Se}/(\text{S}+\text{Se})$ atomic ratio, $\text{Sb}_2(\text{S},\text{Se})_3$ solar cells can break the 10% bottleneck efficiency^[5, 6], which is recorded in the record-efficiency cells table collected by AMOLF (Fig. 1(c)), SbSSe stands for $\text{Sb}_2(\text{S},\text{Se})_3$ solar cells).

Because of the unique quasi-one-dimensional (Q1D) structure, the suitably oriented crystal is critical for efficient charge transport, which is quite different from the three-dimensional (3D) absorbers. In this case, vapor deposition methods, like rapid thermal evaporation (RTE), vapor transport deposition (VTD), closed-space sublimation (CSS), show strong ability to tune the crystal orientation^[4, 7–9]. The high-temperature and low-pressure reactive system enables the fast grain growth, thus kinetically facilitating tilted $(\text{Sb}_4\text{S}(\text{e})_6)_n$ ribbons on the substrate. However, it was observed that although the favorable

orientation was obtained in high percentage, the efficiency did not show great improvement. This causes new concerns regarding the efficiency improvement in this class of solar cells^[10–12]. Further investigations on the materials and device characteristics generate new understanding on fundamental issues associated mainly with the microstructures of antimony selenosulfide.

It is generally accepted that the V_{oc} loss in antimony selenosulfide solar cells is one of the critical factors impeding the efficiency improvement. This deficit is usually ascribed to the defects which lead to increased recombination and dark current^[13]. Nonetheless, Yang *et al.* recently demonstrated that the intrinsically self-trapping in Sb_2S_3 film is primarily responsible for this substantial energy loss^[10]. The spectroscopic study of excited-state carrier properties suggests that the lattice deformation in this film gives rise to self-trapped excitons and thus transient defect state in bandgap (Fig. 1(d)). With this energy loss, the maximum V_{oc} is limited to ~0.8 V for Sb_2S_3 solar cells, which matches the obtained top V_{oc} of 0.8 V in Ref. [14]. This finding pointed out that the suppression of self-trapping effect is able to essentially increase the device efficiency. Plausibly, further investigating similar phenomenon in the alloy-type $\text{Sb}_2(\text{S},\text{Se})_3$ and pure selenide Sb_2Se_3 would be much interesting and significant for understanding the basic properties of this class Q1D materials and efficiency improvement.

The Q1D structure was also found to cause microstructure dislocations. Recently, Li *et al.* demonstrated that the stress generated during fast grain growth in achieving preferred [hk1]-oriented Sb_2Se_3 film brings forth the dislocations (Fig. 1(e)). This structure characteristic results in low carrier mobility and carrier density even in films with favorable orientation, thus limiting the efficiency improvement^[11]. According to the detailed measurement, the majority carrier mobility in Sb_2S_3 and Sb_2Se_3 exhibits orders of magnitude lower than that in $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe). Therefore, developing advanced process to delicately controlling over the crystal growth becomes essential for obtaining high-quality antimony chalcogenide absorber films.

To date, highly efficient $\text{Sb}_2(\text{S},\text{Se})_3$ solar cells are primarily obtained by using CdS as the electron-transporting material (ETM). Most recently, a few theoretical studies were conducted to analyze the interfacial properties and in turn provide resolved strategies^[12, 15]. Williams *et al.* indicated that the unstable $\text{Sb}_2\text{Se}_3/\text{CdS}$ interface inevitably led to Sb and Se diffusing into CdS layer, thus deteriorating the Sb_2Se_3 layer and forming interfacial voids (Fig. 1(f))^[12]. As a consequence, sub-

Correspondence to: T Chen, tchenmse@ustc.edu.cn; L M Ding, ding@nanoctr.cn

Received 30 APRIL 2021.

©2021 Chinese Institute of Electronics

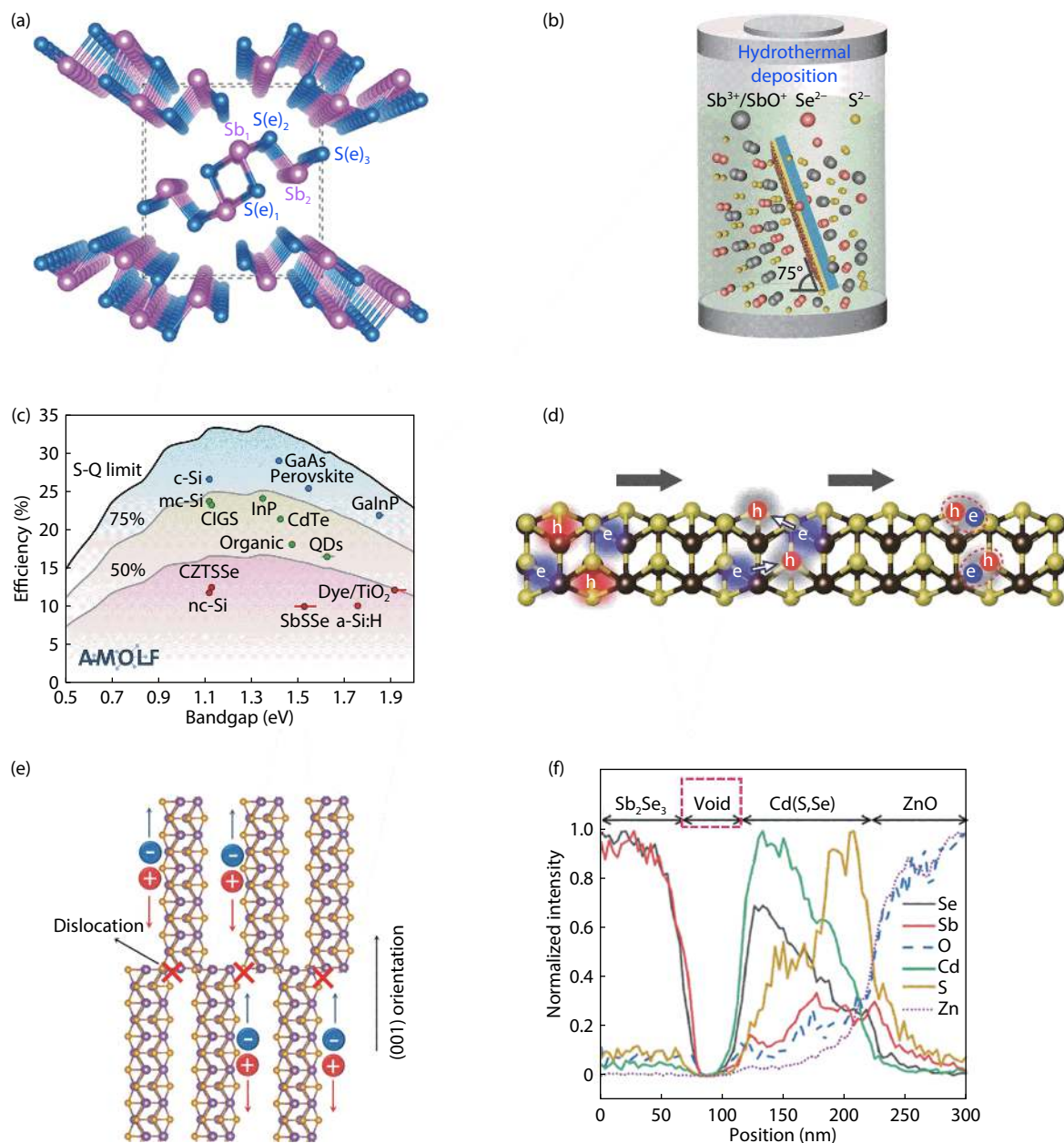


Fig. 1. (Color online) (a) Crystal structure of $\text{Sb}_2(\text{S,Se})_3$. (b) Schematic for the hydrothermal deposition of $\text{Sb}_2(\text{S,Se})_3$ in an autoclave, Copyright 2020, Springer Nature^[5]. (c) Shockley-Queisser limit (black line) achieved by record-efficiency cells, grey lines showing 75% and 50% of the limit, Copyright 2020, <https://www.lmpv.nl/sq/>. (d) Two-step formation process of self-trapped excitons (STEs) in Sb_2S_3 ; hole is self-trapped first and then electron is captured by trapped hole to form STE, Copyright 2019, Springer Nature^[10]. (e) Schematic diagram for the carrier transport near the dislocations along (001) orientation of Sb_2Se_3 , Copyright 2021, John Wiley and Sons^[11]. (f) EDX line scan for sample $\text{Sb}_2\text{Se}_3/\text{CdS}$ (Sb_2Se_3 from CSS approach), Copyright 2020, American Chemical Society^[12].

stantial interfacial defects were generated. This phenomenon becomes particularly serious in films from high-temperature deposition process. Even in $\text{Sb}_2(\text{S,Se})_3$ film made with low-temperature hydrothermal deposition, a simulation study showed that the interface recombination between CdS and $\text{Sb}_2(\text{S,Se})_3$ still gave rise to large V_{oc} loss. Optimistically, seeking ideal ETM/ $\text{Sb}_2(\text{S,Se})_3$ junction with favourable lattice coupling and band alignment is expected to improve efficiency^[15].

In summary, the deposition method, the film quality, the grain size, and the defect density are critical factors determining the performance for $\text{Sb}_2(\text{S,Se})_3$ solar cells. How to reduce the defects, to optimize ETM/ $\text{Sb}_2(\text{S,Se})_3$ interface, to increase charge mobility, to reduce V_{oc} loss, thus enhancing the

device efficiency, is the mission in developing this new solar technology.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (22005293, U19A2092), the China Postdoctoral Science Foundation (BH2060000144), and the National Key Research and Development Program of China (2019YFA0405600). L. Ding thanks the National Key Research and Development Program of China (2017YFA0206600) and the National Natural Science Foundation of China (51773045, 21772030, 51922032, 21961160720).

References

- [1] Lei H W, Chen J J, Tan Z J, et al. Review of recent progress in antimony chalcogenide-based solar cells: materials and devices. *Sol RRL*, 2019, 3, 1900026
- [2] Deng H, Zeng Y Y, Ishaq M, et al. Quasiepitaxy strategy for efficient full-inorganic Sb_2S_3 solar cells. *Adv Funct Mater*, 2019, 29, 1901720
- [3] Wu C Y, Lian W T, Zhang L J, et al. Water additive enhanced solution processing of alloy $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ -based solar cells. *Sol RRL*, 2020, 4, 1900582
- [4] Wang L, Li D B, Li K H, et al. Stable 6%-efficient Sb_2Se_3 solar cells with a ZnO buffer layer. *Nat Energy*, 2017, 2, 17046
- [5] Tang R F, Wang X M, Lian W T, et al. Hydrothermal deposition of antimony selenosulfide thin films enables solar cells with 10% efficiency. *Nat Energy*, 2020, 5, 587
- [6] Wang X M, Tang R F, Jiang C H, et al. Manipulating the electrical properties of $\text{Sb}_2(\text{S}, \text{Se})_3$ film for high-efficiency solar cell. *Adv Energy Mater*, 2020, 10, 2002341
- [7] Wen X X, Chen C, Lu S C, et al. Vapor transport deposition of antimony selenide thin film solar cells with 7.6% efficiency. *Nat Commun*, 2018, 9, 2179
- [8] Li Z Q, Liang X Y, Li G, et al. 9.2%-efficient core-shell structured antimony selenide nanorod array solar cells. *Nat Commun*, 2019, 10, 125
- [9] Zhou Y, Wang L, Chen S Y, et al. Thin-film Sb_2Se_3 photovoltaics with oriented one-dimensional ribbons and benign grain boundaries. *Nat Photonics*, 2015, 9, 409
- [10] Yang Z L, Wang X M, Chen Y Z, et al. Ultrafast self-trapping of photoexcited carriers sets the upper limit on antimony trisulfide photovoltaic devices. *Nat Commun*, 2019, 10, 4540
- [11] Li J J, Huang J L, Li K H, et al. Defect-resolved effective majority carrier mobility in highly anisotropic antimony chalcogenide thin-film solar cells. *Sol RRL*, 2021, 5, 2000693
- [12] Williams R E, Ramasse Q M, McKenna K P, et al. Evidence for self-healing benign grain boundaries and a highly defective Sb_2Se_3 -CdS interfacial layer in Sb_2Se_3 thin-film photovoltaics. *ACS Appl Mater Interfaces*, 2020, 12, 21730
- [13] Chen C, Tang J. Open-circuit voltage loss of antimony chalcogenide solar cells: status, origin, and possible solutions. *ACS Energy Lett*, 2020, 5, 2294
- [14] Maiti A, Chatterjee S, Pal A J. Sulfur-vacancy passivation in solution-processed Sb_2S_3 thin films: Influence on photovoltaic interfaces. *ACS Appl Energy Mater*, 2020, 3, 810

- [15] Ayala-Mató F, Vigil-Galán O, Nicolás-Marín M M, et al. Study of loss mechanisms on $\text{Sb}_2(\text{S}_{1-x}\text{Se}_x)_3$ solar cell with n-i-p structure: Toward an efficiency promotion. *Appl Phys Lett*, 2021, 118, 73903



Rongfeng Tang received her PhD degree in 2019 from University of Science and Technology of China (USTC) under the supervision of Professor Tao Chen. Currently she is a postdoc in Tao Chen group. Her research focuses on antimony chalcogenides semiconductors and devices.



Tao Chen obtained his PhD degree from Nanyang Technological University, Singapore, in 2010. In 2011, he joined Department of Physics, Chinese University of Hong Kong as a research assistant professor. Since 2015, he has been working in Department of Materials Science and Engineering, University of Science and Technology of China as a full professor. His work focuses on metal chalcogenides solar cells.



Liming Ding got his PhD from University of Science and Technology of China (was a joint student at Changchun Institute of Applied Chemistry, CAS). He started his research on OSCs and PLEDs in Olle Inganäs Lab in 1998. Later on, he worked at National Center for Polymer Research, Wright-Patterson Air Force Base and Argonne National Lab (USA). He joined Konarka as a Senior Scientist in 2008. In 2010, he joined National Center for Nanoscience and Technology as a full professor. His research focuses on innovative materials and devices. He is RSC Fellow, the nominator for Xplorer Prize, and the Associate Editors for Science Bulletin and Journal of Semiconductors.