Supplementary Information

A Comprehensive Insight into Deep-Level Defect Engineering in Antimony Chalcogenide Solar Cells

Swapnil Barthwal, Siddhant Singh, Abhishek K. Chauhan, Nimitha S. Prabhu, Akila G. Prabhudessai, and K. Ramesh✉

Department of Physics, Indian Institute of Science, Bengaluru-560012, Karnataka, India.
✉*kramesh@iisc.ac.in*

Table S1: Device architecture, novelty, and performance parameters of the state-of-the-art Sb_2Se_3, $Sb_2(S,Se)_3$, and Sb_2S_3 solar cells, fabricated via different routes.

Absorber layer	Deposition technique	Device architecture	Novelty	Device parameters				Ref.
				Voc (mV)	Jsc (mA cm-2)	FF (%)	PCE (%)	
Sb_2Se_3	Chemical bath deposition (CBD)	FTO/CdS/Sb_2Se_3/Spiro-OMeTAD/Au	Novel additive-assisted CBD for synthesis of Sb_2Se_3 thin films, with superior morphological, electrical, and defect properties	467	33.52	67.64	10.57	[1]
	Injection vapor deposition (IVD)	Mo/$MoSe_2$/Sb_2Se_3/CdS/i-ZnO/Al:ZnO/Au	Strong *[hk1]*-oriented growth, high crystallinity, and minimal deep level defect density in deposited Sb_2Se_3 film	488	30.86	67.19	10.12	[2]
	Close space sublimation (CSS)	Mo/$MoSe_2$/Sb_2Se_3/TiO_2/CdS/i-ZnO/Al:ZnO/Ag	high-quality, *[001]*-oriented Sb_2Se_3 nanorod arrays, for improved photon harvesting and charge-carrier extraction	400	32.58	70.3	9.2	[3]
	Vapor Transport Deposition (VTD)	ITO/CdS/Sb_2Se_3/CuSCN/Au	Cu diffusion into Sb_2Se_3, grain boundary inversion	423	30.8	57.0	7.4	[4]
	VTD	PI/ITO/CdS/Sb_2Se_3/Au	Ultraflexible solar	415	25.5	58.0	6.13	[5]

			cell, high bending tolerance and stability, 25 cm^{-2} minimodule powered IoT devices, LED and electromotors					
	VTD+Selenization	Mo/Sb_2Se_3/CdS/ITO/Ag	Combination of VTD and post selenisation lead to highly *[hk1]*-oriented, compact and stoichiometric Sb_2Se_3 films with low defect density at bulk and interfaces	513	24.56	58.74	7.40	[6]
	Sputtering + Selenization	Mo/Sb_2Se_3/CdS/ITO/Ag	Self-assembled growth of high quality Sb_2Se_3 films	504	24.91	54.47	6.84	[7]
			Post-annealing treatment of CdS/Sb_2Se_3 heterojunction using rapid thermal processing, suppression of recombination at interface and space charge region	520	27.8	59.8	8.64	[8]
	Close Space Sublimation (CSS)	FTO/TiO_2/Sb_2Se_3/spiro-OMeTAD/Au	V-shaped graded bandgap in the $Sb_2(S,Se)_3$ film, produced by co-sublimation of Sb_2Se_3 and Sb_2S_3	451	29.85	59.7	8.03	[9]
		PI/Mo/Sb_2Se_3/CdS/ZnO/Al:ZnO/Ag	Ultraflexible solar cell, 5 nm thick PbSe interlayer at Mo/Sb_2Se_3 interface, suppression of *[hk0]*-oriented grains, suppression of back contact barrier and bulk defects in absorber	452	27.0	64.3	8.43	[10]
$Sb_2(S,Se)_3$	Hydrothermal	FTO/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au	Ethanol assisted additive hydrothermal route, to synthesize $Sb_2(S,Se)_3$ films with low defect density and improved morphology	630	25.27	67.35	10.75	[11]
		FTO/Zn(O,S)/CdS/Sb_2(S,Se	Alkali metal fluoride	673	23.7	66.8	10.7	[12]

		$)_3$/Spiro-OMeTAD/Au	(NaF, KF, RbF, CsF) assisted solution post treatment of $Sb_2(S,Se)_3$ film to improve crystallinity, conductivity, and band alignment					
		FTO/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD)/Au	Synthesis of high-quality $Sb_2(S,Se)_3$ films by employing Ethylenediaminetetra acetic acid (EDTA) as a strong coordination additive, to control the nucleation and growth process	664	23.8	66.3	10.5	[13]
		FTO/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au	Hydrazine hydrate (N_2H_4) solution assisted post-treatment to modify CdS ETL, removal of residual Cd oxychlorides, improving CdS/$Sb_2(S,Se)_3$ interfacial band alignment	678	23.63	66.07	10.3	[14]
		FTO/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au	NH_4F additive to regulate the band gradient in the $Sb_2(S,Se)_3$ and modify CdS/$Sb_2(S,Se)_3$ interface	630	24.76	65.95	10.28	[15]
		FTO/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au	Thermally evaporated, up-scalable, stable and inorganic MnS as HTL, to potentially substitute Spiro-OMeTAD	646	24.29	64.5	10.14	[16]
		FTO/CdS/$Sb_2(S,Se)_3$/MnS/Au		655	22.98	64.2	9.67	
		FTO/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au	Novel deposition strategy for regulating Se/S ratio, improving morphology and passivate defects in $Sb_2(S,Se)_3$ films	630	23.7	67.7	10.10	[17]
		FTO/SnO_2/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au	Novel (and low cost) precursor sodium	551	26.01	70.1	10.05	[18]

			selenosulfate (Na_2SeSO_3) to control S/Se ratio, tuning band gap, and suppressing defect density in $Sb_2(S,Se)_3$ films					
		FTO/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au	Defect monitoring via regulating post deposition annealing parameters	660	22.0	66.2	9.7	19
		FTO/CdS/$Sb_2(S,Se)_3$/DTPThMe-ThTPA /Au	DTPThMe-ThTPA as low cost, highly stable and efficient HTL; electron-rich thiophene moieties coordinate with Sb^{3+} and improve hole transport across $Sb_2(S,Se)_3$/ DTPThMe-ThTPA interface	638	23.18	65.50	9.69	20
		FTO/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au		630	23.31	63.85	9.37	
		FTO/CdS/$Sb_2(S,Se)_3$/Au		529	20.12	52.69	5.60	
		FTO/CdS/$Sb_2(S,Se)_3$/MnS/Au	Inorganic MnS exhibiting better band alignment, stability and hole transport than Spiro-OMeTAD	664	21.26	65.48	9.24	21
		FTO/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au		665	21.65	65.86	9.19	
		FTO/SnO_2/CdS/$Sb_2(S,Se)_3$/Spiro-OMeTAD/Au	Epitaxial growth of *[hk1]*-oriented $Sb_2(S,Se)_3$ films on hexagonal CdS, via solution-based synergistic crystal growth process	604	21.62	70.49	9.21	22
	CSS	FTO/TiO_2/$Sb_2(S,Se)_3$/spiro-OMeTAD/Au	V-shaped graded bandgap in the $Sb_2(S,Se)_3$ film, produced by co-sublimation of Sb_2Se_3 and Sb_2S_3	506	27.81	64.1	9.02	23
Sb_2S_3	Spin coating	FTO/TiO_2/Sb_2S_3/Spiro-OMeTAD/Au	$SbCl_3$ treatment on Sb_2S_3 film, passivation of surface defects on Sb_2S_3 layer	720	17.24	57.18	7.1	24
			$ZnCl_2$ treatment on TiO_2 layer, improvement in electron extraction at TiO_2/Sb_2S_3 interface	650	17.69	61.61	7.08	25
	Chemical bath deposition	FTO/CdS/Sb_2S_3/Spiro-OMeTAD/Au	Multiple S-source to accelerate S^{2-} release,	757	17.41	60.48	8.0	26

	(CBD)		formation of S-rich Sb_2S_3 films					
		$FTO/TiO_2/Sb_2S_3/PCPDTBT$ (PCBM)/Au	Thioacetamide treatment of as deposited Sb_2S_3 films, passivation of surface defects	711	16.1	65	7.5	[27]
	Hydrothermal	$ITO/TiO_2/CdS/Sb_2S_3/C$	Liquid medium annealing strategy, favourable *[041]/[141]* oriented grain growth	718	17.12	58.8	7.23	[28]

References

1. Zhao, Y.; Wang, S.; Li, C.; Che, B.; Chen, X.; Chen, H.; Tang, R.; Wang, X.; Chen, G.; Wang, T.; Gong, J.; Chen, T.; Xiao, X.; Li, J. Regulating Deposition Kinetics via a Novel Additive-Assisted Chemical Bath Deposition Technology Enables Fabrication of 10.57%-Efficiency Sb 2 Se 3 Solar Cells. *Energy Environ. Sci.* **2022**, *15* (12), 5118–5128. https://doi.org/10.1039/D2EE02261C.
2. Duan, Z.; Liang, X.; Feng, Y.; Ma, H.; Liang, B.; Wang, Y.; Luo, S.; Wang, S.; Schropp, R. E. I.; Mai, Y.; Li, Z. Sb 2 Se 3 Thin-Film Solar Cells Exceeding 10% Power Conversion Efficiency Enabled by Injection Vapor Deposition Technology. *Adv. Mater.* **2022**, *34* (30), 2202969. https://doi.org/10.1002/adma.202202969.
3. Li, Z.; Liang, X.; Li, G.; Liu, H.; Zhang, H.; Guo, J.; Chen, J.; Shen, K.; San, X.; Yu, W.; Schropp, R. E. I.; Mai, Y. 9.2%-Efficient Core-Shell Structured Antimony Selenide Nanorod Array Solar Cells. *Nat. Commun.* **2019**, *10* (1), 125. https://doi.org/10.1038/s41467-018-07903-6.
4. Li, K.; Wang, S.; Chen, C.; Kondrotas, R.; Hu, M.; Lu, S.; Wang, C.; Chen, W.; Tang, J. 7.5% n–i–p Sb 2 Se 3 Solar Cells with CuSCN as a Hole-Transport Layer. *J. Mater. Chem. A* **2019**, *7* (16), 9665–9672. https://doi.org/10.1039/C9TA01773A.
5. Li, K.; Li, F.; Chen, C.; Jiang, P.; Lu, S.; Wang, S.; Lu, Y.; Tu, G.; Guo, J.; Shui, L.; Liu, Z.; Song, B.; Tang, J. One-Dimensional Sb2Se3 Enabling Ultra-Flexible Solar Cells and Mini-Modules for IoT Applications. *Nano Energy* **2021**, *86* (April), 106101. https://doi.org/10.1016/j.nanoen.2021.106101.
6. Liang, G.; Chen, M.; Ishaq, M.; Li, X.; Tang, R.; Zheng, Z.; Su, Z.; Fan, P.; Zhang, X.; Chen, S. Crystal Growth Promotion and Defects Healing Enable Minimum Open-Circuit Voltage Deficit in Antimony Selenide Solar Cells. *Adv. Sci.* **2022**, *9* (9), 2105142. https://doi.org/10.1002/advs.202105142.
7. Liang, G.-X.; Luo, Y.-D.; Chen, S.; Tang, R.; Zheng, Z.-H.; Li, X.-J.; Liu, X.-S.; Liu, Y.-K.; Li, Y.-F.; Chen, X.-Y.; Su, Z.-H.; Zhang, X.-H.; Ma, H.-L.; Fan, P. Sputtered and Selenized Sb2Se3 Thin-Film Solar Cells with Open-Circuit Voltage Exceeding 500 MV. *Nano Energy* **2020**, *73*, 104806. https://doi.org/10.1016/j.nanoen.2020.104806.
8. Tang, R.; Chen, S.; Zheng, Z.; Su, Z.; Luo, J.; Fan, P.; Zhang, X.; Tang, J.; Liang, G. Heterojunction Annealing Enabling Record Open-Circuit Voltage in Antimony Triselenide Solar Cells. *Adv. Mater.* **2022**, *34* (14), 2109078. https://doi.org/10.1002/adma.202109078.
9. Liu, C.; Wu, S.; Gao, Y.; Feng, Y.; Wang, X.; Xie, Y.; Zheng, J.; Zhu, H.; Li, Z.; Schropp, R. E. I.; Shen, K.; Mai, Y. Band Gap and Defect Engineering for High-Performance Cadmium-free Sb 2 (S,Se) 3 Solar Cells and Modules. *Adv. Funct. Mater.* **2022**, *32* (49), 2209601. https://doi.org/10.1002/adfm.202209601.
10. Liang, X.; Feng, Y.; Dang, W.; Huang, H.; Wang, X.; Guo, Y.; Shen, K.; Schropp, R. E. I.; Li, Z.; Mai, Y. High-Efficiency Flexible Sb 2 Se 3 Solar Cells by Back Interface and Absorber Bulk Deep-Level Trap Engineering. *ACS Energy Lett.* **2023**, *8* (1), 213–221.

https://doi.org/10.1021/acsenergylett.2c02066.
11. Chen, X.; Che, B.; Zhao, Y.; Wang, S.; Li, H.; Gong, J.; Chen, G.; Chen, T.; Xiao, X.; Li, J. Solvent-Assisted Hydrothermal Deposition Approach for Highly-Efficient Sb 2 (S,Se) 3 Thin-Film Solar Cells. *Adv. Energy Mater.* **2023**. https://doi.org/10.1002/aenm.202300391.
12. Zhao, Y.; Wang, S.; Jiang, C.; Li, C.; Xiao, P.; Tang, R.; Gong, J.; Chen, G.; Chen, T.; Li, J.; Xiao, X. Regulating Energy Band Alignment via Alkaline Metal Fluoride Assisted Solution Post-Treatment Enabling Sb 2(S,Se)3 Solar Cells with 10.7% Efficiency. *Adv. Energy Mater.* **2022**, *12* (1), 2103015. https://doi.org/10.1002/aenm.202103015.
13. Wang, X.; Tang, R.; Jiang, C.; Lian, W.; Ju, H.; Jiang, G.; Li, Z.; Zhu, C.; Chen, T. Manipulating the Electrical Properties of Sb2(S,Se)3 Film for High-Efficiency Solar Cell. *Adv. Energy Mater.* **2020**, *10* (40), 2002341. https://doi.org/10.1002/aenm.202002341.
14. Li, J.; Zhao, Y.; Li, C.; Wang, S.; Chen, X.; Gong, J.; Wang, X.; Xiao, X. Hydrazine Hydrate-Induced Surface Modification of CdS Electron Transport Layer Enables 10.30%-Efficient Sb 2 (S,Se) 3 Planar Solar Cells. *Adv. Sci.* **2022**, *9* (25), 2202356. https://doi.org/10.1002/advs.202202356.
15. Li, G.; Dong, J.; Xiao, P.; Che, B.; Huang, Y.; Zhang, Y.; Tang, R.; Zhu, C.; Chen, T. Dual Effect of NH4F Additive in the Hydrothermal Deposition of Antimony Selenosulfide Thin Film for High-Performance Solar Cells. *Sci. China Mater.* **2022**, *65* (12), 3411–3417. https://doi.org/10.1007/s40843-022-2066-5.
16. Qian, C.; Li, J.; Sun, K.; Jiang, C.; Huang, J.; Tang, R.; Green, M.; Hoex, B.; Chen, T.; Hao, X. 9.6%-Efficient All-Inorganic Sb 2 (S,Se) 3 Solar Cells with a MnS Hole-Transporting Layer. *J. Mater. Chem. A* **2022**, *10* (6), 2835–2841. https://doi.org/10.1039/D1TA09913B.
17. Tang, R.; Wang, X.; Lian, W.; Huang, J.; Wei, Q.; Huang, M.; Yin, Y.; Jiang, C.; Yang, S.; Xing, G.; Chen, S.; Zhu, C.; Hao, X.; Green, M. A.; Chen, T. Hydrothermal Deposition of Antimony Selenosulfide Thin Films Enables Solar Cells with 10% Efficiency. *Nat. Energy* **2020**, *5* (8), 587–595. https://doi.org/10.1038/s41560-020-0652-3.
18. Dong, J.; Liu, H.; Cao, Z.; Liu, Y.; Bai, Y.; Chen, M.; Liu, B.; Wu, L.; Luo, J.; Zhang, Y.; Liu, S. (Frank). Low-Cost Antimony Selenosulfide with Tunable Bandgap for Highly Efficient Solar Cells. *Small* **2022**, 2206175. https://doi.org/10.1002/smll.202206175.
19. Che, B.; Cai, Z.; Xiao, P.; Li, G.; Huang, Y.; Tang, R.; Zhu, C.; Yang, S.; Chen, T. Thermally Driven Point Defect Transformation in Antimony Selenosulfide Photovoltaic Materials. *Adv. Mater.* **2022**, 2208564. https://doi.org/10.1002/adma.202208564.
20. Jiang, C.; Zhou, J.; Tang, R.; Lian, W.; Wang, X.; Lei, X.; Zeng, H.; Zhu, C.; Tang, W.; Chen, T. 9.7%-Efficient Sb 2 (S,Se) 3 Solar Cells with a Dithieno[3,2- B : 2′,3′- d]Pyrrole-Cored Hole Transporting Material. *Energy Environ. Sci.* **2021**, *14* (1), 359–364. https://doi.org/10.1039/D0EE02239J.
21. Wang, S.; Zhao, Y.; Yao, L.; Li, C.; Gong, J.; Chen, G.; Li, J.; Xiao, X. Efficient and Stable All-Inorganic Sb2(S, Se)3 Solar Cells via Manipulating Energy Levels in MnS Hole Transporting Layers. *Sci. Bull.* **2022**, *67* (3), 263–269. https://doi.org/10.1016/j.scib.2021.11.012.
22. Jin, X.; Fang, Y.; Salim, T.; Feng, M.; Yuan, Z.; Hadke, S.; Sum, T. C.; Wong, L. H. Controllable Solution-Phase Epitaxial Growth of Q1D Sb 2 (S,Se) 3 /CdS Heterojunction Solar Cell with 9.2% Efficiency. *Adv. Mater.* **2021**, *33* (44), 2104346. https://doi.org/10.1002/adma.202104346.
23. Liu, C.; Wu, S.; Gao, Y.; Feng, Y.; Wang, X.; Xie, Y.; Zheng, J.; Zhu, H.; Li, Z.; Schropp, R. E. I.; Shen, K.; Mai, Y. Band Gap and Defect Engineering for High-Performance Cadmium-free Sb 2 (S,Se) 3 Solar Cells and Modules. *Adv. Funct. Mater.* **2022**, *32* (49), 2209601. https://doi.org/10.1002/adfm.202209601.
24. Han, J.; Wang, S.; Yang, J.; Guo, S.; Cao, Q.; Tang, H.; Pu, X.; Gao, B.; Li, X. Solution-Processed Sb2S3 Planar Thin Film Solar Cells with a Conversion Efficiency of 6.9% at an Open Circuit Voltage of 0.7 V Achieved via Surface Passivation by a SbCl3 Interface Layer. *ACS Appl. Mater. Interfaces* **2020**, *12* (4), 4970–4979. https://doi.org/10.1021/acsami.9b15148.
25. Han, J.; Pu, X.; Zhou, H.; Cao, Q.; Wang, S.; He, Z.; Gao, B.; Li, T.; Zhao, J.; Li, X. Synergistic Effect through the Introduction of Inorganic Zinc Halides at the Interface of TiO 2

and Sb 2 S 3 for High-Performance Sb 2 S 3 Planar Thin-Film Solar Cells. *ACS Appl. Mater. Interfaces* **2020**, *12* (39), 44297–44306. https://doi.org/10.1021/acsami.0c11550.

26. Wang, S.; Zhao, Y.; Che, B.; Li, C.; Chen, X.; Tang, R.; Gong, J.; Wang, X.; Chen, G.; Chen, T.; Li, J.; Xiao, X. A Novel Multi-Sulfur Source Collaborative Chemical Bath Deposition Technology Enables 8%-Efficiency Sb 2 S 3 Planar Solar Cells. *Adv. Mater.* **2022**, *34* (41), 2206242. https://doi.org/10.1002/adma.202206242.
27. Choi, Y. C.; Lee, D. U.; Noh, J. H.; Kim, E. K.; Seok, S. Il. Highly Improved Sb2S3 Sensitized-Inorganic-Organic Heterojunction Solar Cells and Quantification of Traps by Deep-Level Transient Spectroscopy. *Adv. Funct. Mater.* **2014**, *24* (23), 3587–3592. https://doi.org/10.1002/adfm.201304238.
28. Yao, L.-Q.; Lin, L.-M.; Huang, Z.-P.; Mao, Y.; Li, H.; Lin, W.-W.; Chen, S.-Y.; Huang, Z.-G.; Li, J.-M.; Chen, G.-L. A Liquid Medium Annealing Strategy for Highly [041]/[141]-Oriented Planar Antimony Sulfide Solar Cells with 7.23% Efficiency. *Nano Energy* **2023**, *106*, 108064. https://doi.org/10.1016/j.nanoen.2022.108064.
29. Li, J. V. Deep Level Transient Spectroscopy Characterization without the Arrhenius Plot. *Rev. Sci. Instrum.* **2021**, *92* (2). https://doi.org/10.1063/5.0039555.
30. Whiting, P. G.; Jones, K. S.; Hirschman, K. D.; Senawiratne, J.; Moll, J.; Manley, R. G.; Couillard, J. G.; Kosik Williams, C. A. Peak Shape Analysis of Deep Level Transient Spectra: An Alternative to the Arrhenius Plot. *J. Mater. Res.* **2019**, *34* (10), 1654–1668. https://doi.org/10.1557/jmr.2019.70.
31. Majdi, S.; Gabrysch, M.; Suntornwipat, N.; Burmeister, F.; Jonsson, R.; Kovi, K. K.; Hallén, A. High-Temperature Deep-Level Transient Spectroscopy System for Defect Studies in Wide-Bandgap Semiconductors. *Rev. Sci. Instrum.* **2019**, *90* (6). https://doi.org/10.1063/1.5097755.