

# A review on the device efficiency limiting factors in Sb<sub>2</sub>S<sub>3</sub>-based solar cells and potential solutions to optimize the efficiency

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### Abstract

Thin-film photovoltaics based on earth-abundant and non-toxic Sb<sub>2</sub>S<sub>3</sub> is the frontrunner material in thin-film solar cells due to its broad-band optical response and excellent electrical properties. Nevertheless, a PCE of ~28.64% has been projected for Sb<sub>2</sub>S<sub>3</sub> solar cells, and the highest reported efficiency is ~8%. The poor performance of Sb<sub>2</sub>S<sub>3</sub>-based solar cells is attributed to deep intrinsic traps that enhance recombination. Due to lattice dislocations, surface defects lead to sluggish charge transfer across interfaces and poor charge carrier mobility. A better understanding of the recombination losses in Sb<sub>2</sub>S<sub>3</sub> bulk as an intrinsic layer and interfaces of Sb<sub>2</sub>S<sub>3</sub>-leetron transport and Sb<sub>2</sub>S<sub>3</sub>/hole transport layers and transport mechanisms could lead to significant advancements in device performance. This review discusses the limitations of Sb<sub>2</sub>S<sub>3</sub>-based solar cells based on theoretical and experimental studies, which will pave the way for future improvements in Sb<sub>2</sub>S<sub>3</sub>-based solar cells.

**Keywords**  $Sb_2S_3$  thin film  $\cdot$  Thin-film solar cell  $\cdot$  Limitations of  $Sb_2S_3$ -based solar cells  $\cdot$  Charge carrier recombination

## 1 Introduction

The increasing global energy demand leads to identifying and exploiting environmentally clean and renewable energy sources that can replace conventional energy resources (Suryawanshi et al. 2013; Chang et al. 2012). The solar energy that strikes the earth in one hour is enough to meet the world's annual energy consumption; hence, photovoltaic (PV) technology is at the forefront of converting solar energy into electrical energy at a

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rapid pace (Lewis et al. 2005; Dematage et al. 2014; Boix et al. 2011a; Chang et al. 2010; Manjceevan and Bandara 2016; Akilavasan et al. 2013; Todorov et al. 2013; Giordano et al. 2016; Zhou et al. 2018). The second-generation thin-film solar cells have continued to attract intensive research interest due to their high efficiency/cost ratio among single junction solar cells (Pastuszak and Węgierek 2022). Among them, in PCE, copper gallium indium sulfide (CIGS) and CdTe have achieved 23.4% and 22.0%, respectively (Gloeckler et al. 2013; Bosio et al. 2020; Hirai et al. 2013). Antimony sulfide  $(Sb_2S_3)$  is also one of the best candidates for thin-film solar cells since it possesses non-toxic elements compared to CdTe counterparts. Further, its constituent elements are highly abundant in nature. Sb<sub>2</sub>S<sub>3</sub> exhibits an orthorhombic crystalline structure of the type Pnma. It shows a high absorption coefficient (>  $10^5$  cm<sup>-1</sup>) in the visible region. By generalized gradient approximation,  $Sb_2S_3$  is a direct bandgap semiconductor in the crystalline stibnite form with an energy gap (Eg) of 1.76 eV (Ben Nasr et al. 2011). In direct bandgap semiconductors, the electron-hole pair can be produced relatively quickly due to the same electron momentum of valance and conduction bands. However, producing the electron-hole pairs in an indirect bandgap material with photon and phonon energy is possible. The production of electron-hole pairs in  $Sb_2S_3$  could be faster than Si, whereas Si is an indirect bandgap semiconductor. Although, Si-based solar cells exhibit higher efficiency compared to others. The highest efficiency for  $Sb_2S_3$ -sensitized solar cells is 7.5% for  $Sb_2S_3$  planar (Choi et al. 2014a; Han et al. 2020). However, due to uninvestigated limitations in  $Sb_2S_3$  solar cells, there is a large gap between the highest efficiency and theoretical efficiency of Sb<sub>2</sub>S<sub>3</sub> planar solar cells (Kondrotas et al. 2018).

Although the Sb<sub>2</sub>S<sub>3</sub> is a fascinating light-harvesting material, Sb<sub>2</sub>S<sub>3</sub>-based solar cells' reported performance is inferior to other thin-film-based solar cells (Cai et al. 2020). The highest reported efficiency of ~8% (with an average  $V_{oc}$ , J<sub>sc</sub>, and FF of in the range 400–600 mV, 12–18 mA/cm<sup>2</sup>, and 50–60%, respectively) for Sb<sub>2</sub>S<sub>3</sub> solar cells in planar configuration is much lower than the projected PCE efficiency of ~28% (with  $J_{SC}=22.46 \text{ mA/cm}^2$ ,  $V_{OC}=1.402 \text{ V}$ , FF=91%) under an AM 1.5G spectral irradiance for a single p–n junction with an absorber with 1.7 eV bandgap. Despite the enormous technological developments in the fabrication of defect-free photoactive layers with tunable physical properties, the efficiency of the Sb<sub>2</sub>S<sub>3</sub>-based solar cell devices is far below the theoretical value (Kim et al. 2018; Zimmermann et al. 2015; Zhong et al. 2013; Zhang et al. 2018; Kriisa et al. 2015; Eensalu et al. 2019; Hong et al. 2018; Araújo et al. 2020; Wang et al. 2020). The drive towards enhancing efficiency beyond the value of 7.5% reported in 2014 by Choi et al. (Choi et al. 2014b) forms the basis of this review, which explores the significant and far-reaching theoretical and experimental efforts that have been expended to break this barrier or limit.

## 2 Limitation factors in Sb<sub>2</sub>S<sub>3</sub> solar cell

The limitation factors of planar configuration based on the n-i-p device architecture comprising the ETM/Sb<sub>2</sub>S<sub>3</sub>/HTM configuration is mainly discussed in detail in this section. The device structure and the major charge carrier loss pathways for a n-i-p configuration of Sb<sub>2</sub>S<sub>3</sub> based device are shown in Fig. 1a and b, respectively. These devices use a compact electron transport layer (ETL) coated on FTO and Ag or Au deposits on hole transport layer (HTL) as cathode and anode, respectively. The thin-film of Sb<sub>2</sub>S<sub>3</sub> deposits on the ETM followed by HTL in n-i-p structure. Under illumination, the Sb<sub>2</sub>S<sub>3</sub> on ETM absorbs sunlight



**Fig. 1** a Schematic illustration of device architecture of thin-film  $\text{Sb}_2\text{S}_3$  solar cell. **b** Schematic illustration of photoinduced charge-transfer processes (1) photo excitation of electron under illumination, (2) injection of electron towards Electron Transport Layer (ETL), (3) recombination pathways of excited electron, (4) Hole transport. Where Ec, Ev, Et, Ht and HTM referred the conduction band, the valence band, interface traps, hole traps and hole transport medium, respectively

and produce excited electron in the conduction band and hole in the valance band, followed by charge injections such as electrons and holes in the conduction band and valence band of  $Sb_2S_3$  into ETM and HTL via tunneling process respectively.

Besides the extrinsic factors associated with the device structure and carrier transport limitations circumvented by the band alignment, factors intrinsic to the absorber layer have been found to affect device performance. These effects arise from optical losses or carrier trapping at the defect centers or levels(Zhao et al. 2021). Liping Guo et al. have identified numerous intrinsic defects in the Sb<sub>2</sub>S<sub>3</sub> layer, such as Sb vacancy (V<sub>Sb</sub>), S vacancy (V<sub>S</sub>), S interstitial (S<sub>i</sub>), and Sb and S antisites (Sb<sub>S</sub> and S<sub>Sb</sub>). These defects are the charge trap centers and recombination pathways (Guo et al. 2019). Therefore, the poor performance of Sb<sub>2</sub>S<sub>3</sub> in these types of solar devices can be attributed primarily to intrinsically formed traps that enhance charge carrier recombination in bulk and at the surface/interface. However, it should be noted that the surface defect states can lead to longer carrier lifetime at interfaces and poor charge carrier mobility due to lattice dislocations and topological defects (Zeng et al. 2020; Mahuli et al. 2020; Chen and Tang 2020).

Efficiency enhancement can be accomplished through augmentation of the photon absorption. Several strategies have been explored, such as plasmonic-based nanostructures or quantum confinement methods that promote multiple exciton generation(Catchpole and Polman 2008; Ellingson et al. 2005). In this respect, quantum dots of  $Sb_2S_3$  have been implemented in quantum dot-sensitized solar cells with 1.61% and 3.14% photoconversion efficiencies. More detailed discussions on this aspect can be found in Liang et al. (2018); Hsieh et al. 2015; Sun et al. 2020). However, compare to other thin-film solar cells and DSSC, only limited research has been conducted on the impact of transport mechanisms on device parameters of Sb<sub>2</sub>S<sub>3</sub>-based solar cells, and the lack of such studies could be the reason(s) for not achieving significant progress on  $Sb_2S_3$  solar cells (Farhana et al. 2023). A better understanding of the recombination losses in Sb<sub>2</sub>S<sub>3</sub> bulk and interfaces of Sb<sub>2</sub>S<sub>3</sub>/ ETL and  $Sb_2S_3$ /HTL, as well as transport mechanisms, could lead to significant advancements in device performance of n-i-p configuration assembled with Sb<sub>2</sub>S<sub>3</sub> as an absorber. Hence, theoretical study and investigation of ultrafast self-trapping of photo-excited carriers may facilitate the development of Sb<sub>2</sub>S<sub>3</sub> thin-film-based solar cells. Several research groups (Cai et al. 2020; Courel et al. 2019; Cao et al. 2020; Xiao et al. 2020; Islam and Thakur 2020) have recently reported on the theoretical or simulation of minority carrier lifetime, interface recombination, and different transport mechanisms of  $Sb_2S_3$  thin-films,

while several other research groups (Christians et al. 2013, 2014; Lee et al. 2013; Yang et al. 2019; Grad et al. 2021; Lian et al. 2021; Li et al. 2021) have reported on the experimental investigation of excited-state carrier dynamics and defect properties in  $Sb_2S_3$ . In this review, we discuss the limitations of  $Sb_2S_3$ -based solar cells based on theoretical and experimental studies, which will pave the way for future improvements in  $Sb_2S_3$ -based photovoltaic solar cell performance.

#### 2.1 Experimental study

The experimental investigation of the critical factors such as the carrier conductivity, lifetime, diffusion coefficient, diffusion length of the exciton, chemical capacitance, recombination resistance, and defects, affects the photoelectric behavior of  $Sb_2S_3$  solar cell is indispensable for the improvement of their performance (Boix et al. 2011a, 2011b). In a recent review, the device performance and the optimization of the structure and morphology of the light-harvesting Sb<sub>2</sub>S<sub>3</sub> layer has been discussed (Farhana et al. 2023). Doping of  $Sb_2S_3$ , surface passivation, band alignment optimization, and defect passivation are the most studied techniques to improve the device's performance (Han et al. 2020; Xiao et al. 2020; Myagmarsereejid et al. 2021; Aliyar Farhana and Bandara 2022; Shang et al. 2016). However, the conversion efficiency of the  $Sb_2S_3$  solar cell remains at 7.5% as the optimization has been mostly limited to the  $Sb_2S_3$  structure and a smaller number of research performed on critical factors such as carrier transport and recombination. Depth analysis of carrier transport and recombination were first reported by (Christians et al. 2013) and (Boix et al. 2011a, 2011b). In an early study by Christian et al., the fate of photogenerated holes and diffusion of holes were investigated by femtosecond transient absorption spectroscopy. It was identified that holes captured by sulfur form a sulfide radical  $(S^{-\bullet})$  in the crystal lattice, and then holes transferred from the  $Sb_2S_3$  absorber to the CuSCN hole conductor with an exponential time constant of 1.68 ns as shown in Fig. 2a. The recombination in  $Sb_2S_3$  is reported to be the main limiting factor in determining PCE performance in Sb<sub>2</sub>S<sub>3</sub>-based solar cells, emphasizing the importance of having a well-crystalline and defect-free Sb<sub>2</sub>S<sub>3</sub> coating or surface treatments to mitigate recombination losses. According to Christian et al., hole transfer across the Sb<sub>2</sub>S<sub>3</sub>-CuSCN interface is critical and must be highly efficient in order to improve solar cell performance because hole accumulation in the absorber species due to slow hole-transfer at the Sb<sub>2</sub>S<sub>3</sub>-HTL interface increases the recombination at the  $TiO_2$ -Sb<sub>2</sub>S<sub>3</sub> interface. (Christians et al. 2013) To mitigate the buildup of holes in Sb<sub>2</sub>S<sub>3</sub>, surface modification at the Sb<sub>2</sub>S<sub>3</sub>/CuSNS interface is vital for the optimization of efficiency.

According to Boix et al., hole transfer across the  $Sb_2S_3$ -HTL interface and hole diffusion in the  $Sb_2S_3$  absorber layer play a significant role in device performance (Boix et al. 2011b). It was clearly demonstrated in their study that minority carrier diffusion length and interfacial hole-transfer are important parameters that limit the device performance for a thicker  $Sb_2S_3$  layer (20–130 nm), whereas interfacial hole-transfer, rather than mobility, is the most important parameter limiting the device performance of a thin  $Sb_2S_3$  layer (Christians et al. 2013, 2014). Hence, for further optimization of these photovoltaic, the importance of having a critical  $Sb_2S_3$  thickness beyond the optimum value in which charges are no longer extracted efficiently has been demonstrated in this study (Boix et al. 2011a). By Impedance spectroscopy (IS) analysis, Boix et al. also demonstrated that lower charge recombination in planar polycrystalline  $Sb_2S_3$  thin-film solar cells could be expected due to lower effective surface area and consequently higher Voc and Jsc (Grad et al. 2021).

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**Fig. 2** a Energy level diagram of  $TiO_2/Sb_2S_3/CuSCN$  ETA solar cell showing transfer of photogenerated holes from the absorber species to the p-type hole conductor, Reproduced with permission, Christians et al. (2013) **b** Filtered high-resolution TEM images (left), electron diffraction patterns (inset of left), and color-coated inverse FFT images from the selected pair of reflection spot red-circled in the FFT images of  $Sb_2S_3$ , The label "T" was used to mark the dislocation core, which points the direction of the additional columns. Reproduced with permission, Li et al. (2021), **c** Schematic diagram of the carrier transport near the dislocations along (001) orientation of  $Sb_2(S,Se)_3$  materials. Reproduced with permission, Li et al. (2021)

However, it is predicted that the increase in hole transport resistance in the HTM is due to the reduction in the screening of charges in holes in planar  $Sb_2S_3$  devices affecting the total series resistance of the cell and reducing the FF (Boix et al. 2011b).

Although carrier mobility is one of the most fundamental electronic parameters influencing overall performance, studies of carrier transport in Sb<sub>2</sub>S<sub>3</sub>-based devices are scarce, and to optimize the device performance of Sb<sub>2</sub>S<sub>3</sub>-based solar cells, the investigation of majority carrier mobility is imperative. The majority carrier transport in a working  $Sb_2S_3$ device has been reported by Li. et al. using the defect-resolved mobility measurement (DRMM) method, in which they reported that even with the preferred [hk1] crystalline orientation, which could be beneficial for better carrier transport, Sb<sub>2</sub>S<sub>3</sub> suffers from low carrier mobility, resulting in high bulk resistance and poor carrier collection efficiency (Li et al. 2021). As the measured conductance of Sb<sub>2</sub>S<sub>3</sub> is low, the corresponding effective majority carrier mobility has been reported to be surprisingly as low as  $10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which has been partly attributed to the high anisotropy ribbon-like structure, that restricts inter-ribbon carrier transport between the (Sb<sub>4</sub>Se<sub>6</sub>)<sub>n</sub> or (Sb<sub>4</sub>S<sub>6</sub>)<sub>n</sub> ribbons due to distortion of the periodic lattice of a one-dimensional crystal which is known as Peierls distortion (Kondrotas et al. 2018; Zhou et al. 2015; Zeng et al. 2016). On the other hand, dislocations which are also predicted to be deep electronic trap states constraining the minority carrier lifetime in  $Sb_2S_3$  grains, have been reported to obstruct the carrier transport path as each dislocation may act as a dead-end for both electron and hole transport (Fig. 2b, c).

To mitigate the formation of dislocations, stress control growth by using advanced growth processes has been suggested (Kondrotas et al. 2018). Since  $Sb_2S_3$  is an orthorhombic crystal structure, there are three independent components of linear dielectric tensor. The dielectric constant ( $\varepsilon$ ) is decreasing with increasing frequency because of decreasing orientation polarization. Due to the interfacial polarization,  $\varepsilon$  reach a constant value at high frequency. The dielectric constant at high frequency was found at 9.29434, 131.547, and

126.892 in x, y, z directions, respectively (Radzwan et al. 2017). Another study reported that the dielectric constant of  $Sb_2S_3$  is 7.08 (Kumar and Kumar 2020). The reported short carrier diffusion length in  $Sb_2S_3$  has been attributed to the higher recombination of excited electrons in  $Sb_2S_3$  n-i-p planar or sensitized structure. The fully depleted absorber has been suggested to mitigate the constraints of fill factor and carrier collection efficiency of  $Sb_2S_3$  solar cells caused by low carrier mobility. As the built-in electric field in the n-i-p device structure is applied to the entire absorber layer, carrier transport efficiency and as a result, power conversion efficiency can be enhanced. Hence, in order to significantly improve the effective carrier mobility of  $Sb_2S_3$  and  $Sb_2Se_3$ , it is critical to not only modify the grain orientation further, but also to reduce crystalline defects within the grains because the dislocations are commonly distributed in the grains.

Li et al. reported that defects (extrinsic or intrinsic) in  $Sb_2S_3$  film detrimentally affects the solar cell performance. By optical deep-level transient spectroscopy investigation, Lian et al., reported three electron traps, E1, E2, and E3 (donor defects), with energy levels of 0.31, 0.60, and 0.69 eV below the conduction band minimum (CBM) in Sb-rich  $Sb_2S_3$ film.(Lian et al. 2021). While in the S-rich Sb<sub>2</sub>S<sub>3</sub> film (Fig. 3a(i)-(ii)), two-hole traps H1 and H2 (acceptor defects) with energy levels of 0.64 and 0.71 eV above the valence band maximum (VBM) were reported. These traps E1, E2, E3, H1, and H2 have been attributed to Sb-interstitial (Sb<sub>i</sub>), S-vacancy (V<sub>S</sub>), Sb<sub>S</sub> antisite, Sb-vacancy (V<sub>Sb</sub>), and S<sub>Sb</sub> antisite defects, respectively (Cai et al. 2020; Guo et al. 2019). It has been reported that defects V<sub>S</sub> and Sb<sub>S</sub> predominant in Sb-rich Sb<sub>2</sub>S<sub>3</sub> whereas V<sub>Sb</sub> (major)and S<sub>Sb</sub> antisite (minor) appear in S-rich conditions, and these defects act as carrier traps/ recombination sites as the energy level of these deep-level defects are more than 0.3 eV far from CBM or VBM(Lian et al. 2021). Traps E2 and E3 in Sb-rich  $Sb_2S_3$  (Table 1), were reported to enhance the charge recombination due to large capture cross-section and high trap density, whereas traps H1 and H2 in S-rich Sb<sub>2</sub>S<sub>3</sub> were found to suppress charge recombination and prolonged the charge carrier lifetime due to small capture cross-section and low trap density. Hence, in-Sb-rich Sb<sub>2</sub>S<sub>3</sub> film, inefficient extraction of trapped photo-excited carriers leads to pinning the electron quasi-Fermi level near traps E2 and E3, whereas in S-rich conditions, the pinning effects are reduced, resulting in improved  $V_{OC}$  pinning effects (Lian et al. 2021). Therefore, the next breakthrough efficiencies of Sb<sub>2</sub>S<sub>3</sub> could be with S-rich Sb<sub>2</sub>S<sub>3</sub> film that suppresses V<sub>Sb</sub> without introducing new deep-level defects. Similarly, Lee et al. reported an interface trap around Ec -1.03 eV below the conduction band edge of Sb<sub>2</sub>S<sub>3</sub> based on deep-level transient spectroscopy (DLTS) analysis and its role as are recombination center for carriers generated from  $Sb_2S_3$  QDs (Fig. 3b). (Lee et al. 2013).

In recent years, Yang et al. and Grad et al., investigated the time-resolved transient absorption (TA) and time-resolved two-photon photoemission (tr-2PPE) measurements to access the major energy loss mechanisms in planar  $Sb_2S_3$  solar cells. It was reported that the experimentally observed excited state carrier lifetimes are barely explainable by an extrinsic defect trapping mechanism caused by extrinsic defects such as surface/interface/ bulk defects. (Yang et al. 2019; Grad et al. 2021) By performing absorption and photoluminescence spectroscopy studies together with time-resolved TA measurements of polycrystalline  $Sb_2S_3$  film and high-quality stoichiometric  $Sb_2S_3$  single crystals, Yang et al., strongly suggested that the losses can be attributed to low charge carrier mobility due to intrinsically self-trapping of photo-excited carriers in  $Sb_2S_3$  by lattice deformation (Yang et al. 2019). As self-trapping is common in materials with small elastic constant, self-trapping is possible with  $Sb_2S_3$  as the calculated elastic constant of  $Sb_2S_3$  is small (~40) (Landau 1933; Koc et al. 2012). As  $Sb_2S_3$  has a soft lattice with quasi-1D crystal structure composed with ( $S_4S_6$ )<sub>n</sub> ribbons stacked with van der Waals interaction, free carriers



**Fig.3** a Schematic of band structure. (i), (ii) Conduction band ( $E_C$ ), valence band ( $E_V$ ), Fermi level ( $E_F$ ), and trap energy level ( $E_T$ ) for Sb-rich and S-rich Sb<sub>2</sub>S<sub>3</sub> films. Reproduced under terms of the CC-BY license, Lian et al. (2021), **b** An illustration of carrier transport from the Sb<sub>2</sub>S<sub>3</sub> QDs to the FTO electrode and carrier capture process into the defect state in the inorganic–organic heterojunction Sb<sub>2</sub>S<sub>3</sub> QD solar cell. Reproduced with permission, Lee et al. (2013) **c** Self-trapping process. a Scheme showing two-step formation process of STEs in Sb<sub>2</sub>S<sub>3</sub>: hole is self-trapped first and then electron is captured by trapped hole to form STE. Reproduced under terms of the CC-BY license, Yang et al. (2019) **d** Relaxation pathways and self-trapping: At  $t_0$  an electron is excited from the VB to the CB due to absorption of a pump photon. In the 1-step process the photogenerated electron–hole pair is immediately trapped by local lattice distortions and forms a self-trapped exciton (STE). In the 2-step process, a free electron and hole are trapped separately within the lattice before they merge to form a STE. The trapping of free charge carriers is marked by red and orange arrows, and charge carrier relaxation is indicated by pink arrows. The measured time constants are indicated. Reproduced under terms of the CC-BY license, Grad et al. (2021).

Table 1	Deep-level defect parameters (trap type, trap energy level ( $E_T$ ), capture cross section ( $\sigma$	), trap	den-
sity (N <sub>T</sub>	), carrier lifetime ( $\tau$ ), shallow donor concentration (N <sub>S</sub> )) of Sb-rich and S-rich Sb <sub>2</sub> S <sub>3</sub> fil	ms. R	epro-
duced w	vith permission Lian et al. (2021)		

Sample	Trap	$E_{T}(eV)$	$\sigma$ (cm <sup>2</sup> )	$N_{T} (cm^{-3})$	$\tau$ (ns)	Ns (cm <sup>-3</sup> )
Sb-rich	$E_1$	$Ec-0.31 \pm 0.02$	$(0.54 - 8.13) \times 10^{-17}$	$(3.75-5.63) \times 10^{14}$	$2.18 \times 10^{3}$	$7.71 \times 10^{16}$
	$E_2$	$\text{Ec-}0.60 \pm 0.02$	$(0.26 - 4.68) \times 10^{-16}$	$(1.57 - 3.31) \times 10^{15}$	$6.46 \times 10^{1}$	
	E <sub>3</sub>	$Ec-0.69 \pm 0.02$	$(0.11 - 1.75) \times 10^{-15}$	$(1.38 - 2.01) \times 10^{15}$	$2.84 \times 10^{1}$	
S-rich	H <sub>1</sub>	$Ec + 0.64 \pm 0.01$	$(0.46 - 1.31) \times 10^{-15}$	$(0.45 - 1.58) \times 10^{15}$	$4.83 \times 10^{1}$	$5.13 \times 10^{16}$
	$H_2$	$\mathrm{Ec} + 0.71 \pm 0.02$	$(0.49 - 1.17) \times 10^{-16}$	$(6.71 - 8.57) \times 10^{14}$	$9.97 \times 10^{2}$	

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can be trapped within potential wells produced by local lattice distortion. Later, Grad et al. confirmed the intrinsically self-trapping states in 1-D Sb<sub>2</sub>S<sub>3</sub> by using time-resolved twophoton photoemission (tr-2PPE) experiments carried out to identify the loss mechanism in the (100) surface of a cleaved  $Sb_2S_3$  single-crystal(Grad et al. 2021). Based on ultrafast relaxation measurements, as shown in Fig. 3c and d, the authors proposed a self-trapping model in which, after photoexcitation of an electron-hole pair, the conduction band minimum (CBM) has been observed in less than 150 fs and self-trapping of free carriers by the depopulation of the CBM within 1.3 ps. Consequently, these electrons in the CBM get trapped by phonons (to form polarons), causing the electrons to slightly lower their energy and form self-trapping of electrons (TE) or captured by trapped holes to form selftrapped excitons (STE). The TE and STE states were reported to be located in the band gap at 0.06 eV and 0.44 eV below the conduction band minimum, respectively, with charge carriers having long lifetimes of 27 ps and 63 ps, respectively. Hence the losses can be attributed to low charge carrier mobility as a result of self-trapped charge carriers in gap states have longer lifetimes. It was found that the trap states are intrinsically formed in 1D material. As the major energy loss process in Sb<sub>2</sub>S<sub>3</sub> has been attributed to self-trapping in  $Sb_2S_3$  due to local lattice distortions and considering the fact that the self-trapping will exist even in a perfect Sb<sub>2</sub>S<sub>3</sub> crystal, the theoretical V<sub>oc</sub> and PCE upper limits have been reduced from 1.4V to 0.8V and 28.6% to 16% respectively(Yang et al. 2019). Hence, as demonstrated by Yang et al. and Grad et al., the self-trapping phenomenon is inevitable in soft-1D Sb<sub>2</sub>S<sub>3</sub> materials but can be minimized by stiffening the elastic properties of Sb<sub>2</sub>S<sub>3</sub> in order to increase the PCE of  $Sb_2S_3$  solar devices (Yang et al. 2019; Grad et al. 2021). On the other hand, as demonstrated by these investigations, self-trapping should also occur in  $Sb_2S_3$ -sensitized photovoltaic devices in addition to extrinsic surface trapping. Further, Han, j. et. Al., in 2021 reported that the steady-state photoluminescence (PL) spectra of different  $Sb_2S_3$  films deposited on quartz substrates and PL emission peaks locate at ca. 737 nm, which is close to the  $Sb_2S_3$  absorption band edge shows lower PL intensity as a result of higher nonradiative recombination owing to the low crystallinity and relatively numerous trap states. Addition of  $[TMA][PF_6]$ , leads to strong PL intensities which is favorable for the crystallinity improvement and defect healing and the PCE efficiency increases from 4.27 to 6.63 (Han et al. 2021).

### 3 Theoretical study

Theoretical calculations have been used to explain and categorize the reason(s) for the reported low efficiencies for  $Sb_2S_3$ -based solar cells, paving the way for future research into the impact of recombination mechanisms on solar cells at both the  $Sb_2S_3$  bulk material and the  $Sb_2S_3$ /buffer layer interface (Jiménez et al. 2018). According to theoretical calculations by Courel et al., the defects have an impact on minority carrier lifetime, buffer/ absorber interface recombination, tunneling enhanced recombination, and recombination due to bulk defects as the major loss mechanisms for the device glass/Au/Sb\_2S\_3/CdS/ZnO/ZnO:Al configuration. (Courel et al. 2019) For their theoretical calculations, the diode ideality factor of 2 has been used as the observed experimental efficiencies are far behind the efficiency values predicted. Ideality factor 1 is taken under the diffusion and radiative recombination mechanisms(Courel et al. 2019).

By simulating each dominant loss mechanism in  $CdS/Sb_2S_3$  interface recombination,  $Sb_2S_3$  non-radiative recombination, and tunneling enhanced recombination at  $Sb_2S_3$  absorber material separately on Voc,  $J_{sc}$  and FF (Courel et al. 2019), (table 2 in Courel et al. (2019)) recombination at Sb<sub>2</sub>S<sub>3</sub> bulk material and CdS/Sb<sub>2</sub>S<sub>3</sub> interface have been identified as the dominant loss mechanism (Courel et al. 2019). Furthermore, since the simulated solar cell parameters based on the defect loss mechanism agree well with the experimentally measured ones (PCE~5.0% and Voc 600–700 mV), the major defects in Sb<sub>2</sub>S<sub>3</sub> were reported to be the limiting factor for device performance. On the other hand, the 11.06% and 18.5% PCE obtained under non-optimized and ideal series/shunt resistance values respectively have mainly attributed to the change in FF from 53.9% (non-ideal conditions) to 83% (ideal conditions) implying that more efforts should be made to optimize series resistance (*R*s), shunt resistance (*R*sh) to overcome the efficiency barrier(Courel et al. 2019). Poor series and shunt resistances have been found to arise as a result of nonideal band alignment, the formation of Schottky contacts, element diffusion, the formation of defects at the semiconductor/metal contact, and poor crystallinity (Fig. 4a).

By performing two-stage modeling for common buffer layers used in  $Sb_2S_3$ -based solar cells, Islam et al. reported a similar loss mechanism and the critical roles of the Rs and Rsh as well as recombination effect for PEC performance (Fig. 4b, c, d) (Islam and Thakur 2020). In addition, it was noted that the optimum thickness of the  $Sb_2S_3$  absorber layer (considering both electronic and optical properties), was highly dependent on the type of buffer layer used, with optimal thicknesses reported to be ~  $1.5-1.8 \,\mu\text{m}$  for Sb<sub>2</sub>S<sub>3</sub>/ZnS while for  $Sb_2S_3/CdS$  and  $Sb_2S_3/TiO_2$  was found to be 2-4 µm. ZnS material is non-toxic compared to CdS material, and the quantum efficiency of thin-film solar cells with CdS buffer layer decline at short wavelengths due to the optical absorption losses from the CdS (Jeon et al. 2016). However, ZnS shows higher optimal transmittance about 95% in visible region (Agrawal et al. 2020). Typical thickness CdS window layer is about 30-80 nm and the less thickness of CdS layer may create pinholes and develop shunting path, leads to lower performance of solar cell (Agrawal et al. 2020). Furthermore, Islam et al. demonstrated the importance of proper band alignment and thus the conduction band offset (CBO) between the absorber and buffer layers for efficient charge flow across the junction to control interfacial recombination in their simulation work, and better PCE performances were predicted with ZnS buffer layers than with CdS(bandgap 2.4 eV) and TiO<sub>2</sub> buffer layers (bandgap 3.2 eV). As shown in Figs. 5a, b, and c, the CBO of ZnS, CdS, and TiO<sub>2</sub> are +0.26, -0.2, and -0.5 eV, respectively, and thus a spike-type CBO has been reported for ZnO, whereas a cliff-type CBO has been reported for CdS and TiO<sub>2</sub>, respectively, and thus, as shown in Fig. 5d and e, electron hole recombination is energetically favorable for cliff and for spiketype CBO having a small CBO i.e. less than +0.04 eV, mobility of holes is not favored



Fig. 4 a Sb<sub>2</sub>S<sub>3</sub> solar cell efficiency as a function of series and shunt resistance values under non-optimized values of Sb<sub>2</sub>S<sub>3</sub> minority carrier lifetime and Sb<sub>2</sub>S<sub>3</sub>/CdS interface recombination speed. Reproduced with permission,[42]; Effect of the thickness of the absorber layer on the performance parameters device for **b** Sb<sub>2</sub>S<sub>3</sub>/ZnS, **c** Sb<sub>2</sub>S<sub>3</sub>/CdS, and **d** Sb<sub>2</sub>S<sub>3</sub>/TiO<sub>2</sub> combination respectively. Reproduced with permission, Islam and Thakur (2020).



**Fig. 5** The band diagram of the device structure and conduction band offset (CBO) at absorber/buffer counterpart interface. **a**–**c** represent device for Sb<sub>2</sub>S<sub>3</sub>/ZnS, Sb<sub>2</sub>S<sub>3</sub>/CdS and Sb<sub>2</sub>S<sub>3</sub>/TiO<sub>2</sub> combination respectively. Reproduced with permission Islam and Thakur (2020). The schematic diagram of **d** the cliff and **e** spike type CBO at the absorber/buffer interface **d** shows that interfacial recombination is more favorable for cliff type junction and **e** shows that interfacial recombination is negligible for spike type junction. **f** Effect of CBO on the recombination current and efficiency of the solar device. Reproduced with permission Islam and Thakur (2020).

while photo-generated electrons can transfer via tunneling process. The spike -type energy level alignment is favorable for defeat the recombination due to the formation of the potential barrier at the interface but too positive CBO leads to high potential barrier at the interface and leads to lower short-circuit current and the solar cell performances(Wang et al. 2022). On the other hand, for efficient charge transfer from  $Sb_2S_3$  to buffer layer, a cliff type CBO is preferred. The bulk defects in the materials and the interface should be optimized owing to the bulk defects act as a trap state leads to charge recombination. Further, based on their overall simulation work, as shown in Fig. 5a, b, c, d, e, f, the need for a spike-type band alignment at the front contact and a high work function metal at the back contact as essential requirements to improve device performance has been identified. Although, they did not consider the interface-modulated doping at the interface.

On the other hand, Cao et al. demonstrated the optimized parameters for each device component through the simulation of a one-dimensional device with an n-i-p planar hetero-junction front contact/ETL/Sb<sub>2</sub>S<sub>3</sub>/HTL/back contact (Fig. 6a, b) (Cao et al. 2020). In the case of ETL, decreasing the  $CBM_{ETL}$  reported to decrease the potential barrier, and even  $Sb_2S_3$  layer's energy band will bend downward, increasing the  $CBM_{ETL}$  beyond -4.0 eV facilitates the electron collection due to the decreased potential barrier, whereas decreasing the  $VBM_{HTL}$  reported to decrease the electric field, facilitating hole collection due to decreased potential barrier. As a result, Cao et al. predicted (Fig. 6b) that an efficient carrier transfer process for  $Sb_2S_3$  as an absorber layer could be achieved by selecting an



**Fig. 6** a Schematic of energy-level diagram of  $Sb_2S_3$  solar cell with a large parameter window for electron transport layers and hole transport layers. Reproduced with permission, Cao et al. (2020), **b** a typical energy level alignment with the optimal band structure of electron transport layer as well as the hole transport layer. Reproduced with permission, Cao et al. (2020), **c** The photovoltaic performance parameters ( $\eta$ ) of the Sb<sub>2</sub>S<sub>3</sub> solar cells with different values of interface defect density at ZnS/Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub>/Cu<sub>2</sub>O heterointerfaces. Reproduced with permission, Xiao et al. (2020), **d** The photovoltaic performance parameters ( $\eta$ ) of the Sb<sub>2</sub>S<sub>3</sub> solar cells with different values of N<sub>t</sub> (corresponding different LD) and thickness of Sb<sub>2</sub>S<sub>3</sub> layer. Reproduced with permission, Xiao et al. (2020), **e** Schematic illustration of the strategy for efficient p-type doping in Sb<sub>2</sub>S<sub>3</sub>. E<sub>F</sub> in this figure means the Fermi level Reproduced with permission, Cai et al. (2020)

ETL with a conduction band minimum of -4.4 eV < CBM < -3.2 eV and an HTL with a valence band maximum of -5.2 eV > VBM > -6.4 eV owing to the interfacial potential barrier becoming negligible with appropriate energy levels of both ETL and HTL (Cao et al. 2020). Accordingly, the best PCE of the Sb<sub>2</sub>S<sub>3</sub> cell with the CBM<sub>ETL</sub> and VBM<sub>HTL</sub> is suggested to be -3.5 eV and -6.1 eV, respectively.

By exploring the effect of the relative positions of the  $CBM_{ETL}$  vs. the work function of the front electrode as well as  $VBM_{HTL}$  Vs. the work function of the back contact, the electron and hole collection properties were predicted respectively by Cao et al. in the same study (Cao et al. 2020). Accordingly, a PCE of ~ 14% has been predicted with the  $CBM_{ETL}$  less than – 3.4 eV, and  $\Delta E_{C-F}$  ranging from—1 eV to 0.4 eV, while maintaining the detailed parameters nearly the same. Approximately the same performance has been reported for different VBM<sub>HTL</sub> and  $\Delta E_{V-B}$  values, until the  $\Delta E_{V-B}$  is less than – 0.6 eV. Within the range of the above parameters, when the  $CBM_{ETL}$  is – 3.4 eV,  $\Delta E_{C-F}$  is – 0.3 eV, VBM<sub>HTL</sub> is – 6 eV and  $\Delta E_{V-B}$  is –0.1 eV, a PCE of 15.62% (Voc=1.125 V, Jsc=17.83 mA/cm<sup>2</sup>, FF=77.91%) can be obtained (Cao et al. 2020).

However, Cao et al. has not considered carrier recombination completely in their simulation study, which is one of the major loss mechanisms in  $Sb_2S_3$  solar cells due to various electrically active intrinsic point defects and extrinsic defects in  $Sb_2S_3$  (Cao et al. 2020). Hence, Xiao et al., in their investigation, a numerical simulation has been done on full-inorganic FTO/ ZnS/Sb<sub>2</sub>S<sub>3</sub>/HTLs/Au, solar cell considering different bulk defect densities in bulk  $Sb_2S_3$  as well as ETL/Sb<sub>2</sub>S<sub>3</sub> and  $Sb_2S_3$ /HTL hetero-interfaces (Xiao et al. 2020).

The simulation results shown in Fig. 6c demonstrated the importance of having a proper higher carrier diffusion length than the thickness of the Sb<sub>2</sub>S<sub>3</sub> layer to facilitate the conversion of photogenerated electron-hole pairs to photogenerated current, and it has been noted that the Sb<sub>2</sub>S<sub>3</sub> layer thickness significantly affecting charge collection efficiency in high-defect density region corresponds to short carrier diffusion length. The highest device performance has been predicted at lower values of  $N_t$  (10<sup>15</sup> cm<sup>-3</sup>) and larger values of  $L_D$ (1.6 µm) for an average Sb<sub>2</sub>S<sub>3</sub> thickness of 0.8 µm. On the other hand, it has been demonstrated that improving hetero-junction quality can improve device performance by maintaining a lower interface defect density of ~ 10<sup>9</sup> cm<sup>-2</sup> at both ZnS/Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub>/Cu<sub>2</sub>O interfaces, which could be achieved by improving the hetero-junction quality (Fig. 6d).

Based on the calculated band structure and density of states for Sb<sub>2</sub>S<sub>3</sub>, the conduction band minimum is composed mainly of the Sb 5p and S 3p orbitals an antibonding state of the p-p hybridization, and the VBM is composed mainly of the Sb 5 s and S 3p orbitals in the antibonding states of the s-p hybridization (Cai et al. 2020). The high electrical resistivity due to the presence of intrinsic point defects in  $Sb_2S_3$  is a critical factor that causes the low efficiency and to address the relationship between the resistivity vs. the point defects in  $Sb_2S_3$ . Cai et al., investigated how the intrinsic defect limits the electrical conductivity and a two-step p-Type doping strategy for overcoming the efficiency bottleneck of  $Sb_2S_3$ -based solar cells was proposed (Cai et al. 2020). The formation energy of  $V_{s2}$  and  $V_{s3}$  are similar, and the formation energy of neutral  $V_{s1}$  is lower than that of  $V_{s2}$ and  $V_{S3}$ . When  $V_{S1}$  is ionized to +2 charge state, its formation energy becomes higher than that of  $V_{S2}$  and  $V_{S3}$ . For cation vacancies,  $V_{Sb1}$  and  $V_{Sb2}$  have similar formation energies. From the result of the first-principle calculation, Cai et al. reported that the high-resistivity that limit the performance of  $Sb_2S_3$  results from the compensation between the intrinsic donor, V<sub>S</sub> and acceptors V<sub>Sb</sub>, Sb<sub>S</sub>, and S<sub>Sb</sub> formed due to their comparatively low formation energy pinning of the Fermi level at the middle of the band gap in intrinsic Sb<sub>2</sub>S<sub>3</sub>. The increase in conductivity caused by external p-type doping in intrinsic Sb<sub>2</sub>S<sub>3</sub> was discovered to produce more donor V<sub>S</sub> sites, resulting in many electron carriers and pushing the Fermi level up, making p-type doping difficult to realize. Similarly, external n-type doping in  $Sb_2S_3$  was also found to be difficult to be realized due to the formation of high concentration dominant intrinsic acceptor V<sub>Sb2</sub> during external doping. Hence, Cai et al. proposed a two-step doping strategy that allows for the introduction of p-type dopants later(Cai et al. 2020). As shown in Fig. 6e, donor Vs defects were passivated first with O, then with p-type doping to increase hole carrier concentration and sulfurization of the O-doped Sb<sub>2</sub>S<sub>3</sub> under the S-rich condition to suppress the other p-type limiting and recombination-center donor defects. During O passivation, O is discovered to occupy one (S2) of the two S sites, forming the OS2 defect, which is the main source of hole trap sites, and because OS2 has a low formation energy, the dominant donor VS2 is filled by O. As a result, the Fermi level is reduced to 0.58 eV above the valence band maximum (VBM), allowing the hole carrier concentration and p-type conductivity to increase. However, in the S-rich sulfurization process, S<sub>i</sub> has been identified as the dominant defect, and the Fermi level has been set at approximately 0.58 eV above the VBM due to competition between the dominant donor Si and the dominant acceptor  $S_{Sb2}$ . As a result, after sulfurization, improved p-type conductivity with higher hole concentration has been predicted.

On the other hand, high resistivity that occurs due to pinning of the Fermi level near the mid-gap due to the presence of defects  $V_{Sb}$  and  $V_S$  at deep levels inside the band gap which can trap the charge free carriers in  $Sb_2S_3$  were systematically investigated by using hybrid functional theory by (Zhao et al. 2021) Extrinsic dopants such as Zn, Cu, Ti, Br, and Cl, as well as their complexes with native defects, were also reported in the

same study to control carrier transport in  $Sb_2S_3$ . Zhao et al. clearly demonstrated that Cl/Br and Zn/Cu dopants complexing with native defects can reduce the trapping energy of the native defects, improving carrier transport efficiency. A Cu<sub>sb</sub> acceptor can easily bind with a V<sub>S</sub> donor, forming a neutral Cu<sub>Sb</sub> + V<sub>S</sub> complex that is much more delocalized and difficult to dissociate, as shown in Fig. 7. The doped Cu metal in Sb<sub>2</sub>S<sub>3</sub> films is primarily anchored with sulfur at the surface and grain boundaries, resulting in the formation of single-phase  $Sb_2S_3$  up to 2% Cu-doping concentration and the emergence of a minor CuSbS<sub>2</sub> phase beyond 4% Cu-doping concentration(Lei et al. 2019; Chalapathi et al. 2019).  $Cu_{Sb2} + V_{S3}$  defect levels also become shallower than those of isolated defects due to donor-acceptor coupling, which pushes the electron and hole-trapping levels apart, resulting in the electronic trapping level being closer to the CBM and the hole-trapping level being closer to the VBM, as shown in Fig. 7. As a result, Zhao et al. demonstrated that Fermi level pinning can be eliminated by chemical doping of shallow donors with Cl, Br or shallow acceptors with Zn, Cu, resulting in a higher carrier density and a means to fine-tune the properties of the interface with other components of the solar cell such as the electron-extraction layer and the hole-transport layer. According to the simulation results, Zn and Cl were discovered to be the best dopants for reducing V<sub>Sb</sub> and V<sub>S</sub> defects, respectively, because Zn<sub>Sb</sub> and Cl<sub>S</sub> are much shallower than vacancies ( $V_{Sh}$  and  $V_{S}$ ).



**Fig. 7** Effects of  $Cu_{Sb1}-V_{S1}$  binding on the electron-trapping level of  $V_{S1}$  and the hole-trapping level of  $Cu_{Sb1}$ . **a** and **d** show the (2+/+) electron trapping level of  $V_{S1}$  and the charge density of the trapped electron at  $(V_{S1})^+$ , respectively; **b** and **e** show the (2-/-) hole trapping level of  $Cu_{Sb1}$  and the charge density of the trapped hole at  $(Cu_{Sb1})^-$ , respectively; (c) shows the (0/-) electron-trapping and the (+/0) hole-trapping levels of  $Cu_{Sb1}+V_{S1}$ ; and (f) shows the trapped electron at  $(Cu_{Sb1}+V_{S1})^-$  (upper panel) and the trapped hole at  $(Cu_{Sb1}+V_{S1})^+$  (lower panel). Reproduced with permission, Zhao et al. (2021).

#### 4 Prospective and summary—conclusions and outlook

This review includes a discussion of the limitations of Sb<sub>2</sub>S<sub>3</sub>-based photovoltaic devices using theoretical and experimental study and to set the upper limit and overcome the efficiency barrier of Sb<sub>2</sub>S<sub>3</sub> thin-film-based solar cells paving a new path to improving Sb<sub>2</sub>S<sub>3</sub> performance in the future. In a recent review, it was shown how the morphology and structural changes in  $Sb_2S_3$  thin-films produced using various fabrication techniques and conditions affect solar cell performance(Farhana et al. 2023). It has been noted the formation of finite  $(Sb_4S_6)_n$  ribbon-like structures along the c-axis are common in orthorhombic  $Sb_2S_3$ and the bandgap of  $Sb_2S_3$  reported to vary between 1.56 and 2.25 eV, while the reported conductivity of  $Sb_2S_3$  in room temperature ranges between  $10^{-8}$  and  $10^{-9} \Omega^{-1} \text{ cm}^{-1}$  dependence. ing on the fabrication methods and parameters. The most common factors that have been attributed to the reported poor performance of  $Sb_2S_3$  in solar devices fabricated by different methods are intrinsically formed traps and the presence of surface defect states. The types of defects in  $Sb_2S_3$  and their binding energies and positions within the forbidden region have been explained by DLTS and theoretical investigations (Farhana et al. 2023). The reported poor performance of Sb<sub>2</sub>S<sub>3</sub> in solar devices implies that significant factors such as intrinsically formed traps and the presence of surface defect states, which have been identified as limiting factors for device performance, have not been successfully addressed. As a result, achieving the goal of a 28% efficient Sb<sub>2</sub>S<sub>3</sub> solar cell is a significant challenge due to the large gap between the theoretical predicted and current record  $Sb_2S_3$  device PCE, which necessitates a large number of comprehensive research efforts. However, the lack of such coordinated studies could be one of the reasons for the slow progress on  $Sb_2S_3$  solar cells.

Experimentally it has been shown that major donor defects or electron traps, Sb-S-vacancy ( $V_S$ ), and Sb-antisite, (Sb<sub>S</sub>), appearing in Sb-rich Sb<sub>2</sub>S<sub>3</sub> act as carrier traps/ recombination sites, resulting in electron quasi-Fermi level pinning due to inefficient extraction of trapped photo-excited carriers, whereas acceptor defects or hole traps Sbvacancy (V<sub>Sb</sub>) and S-antisite (S<sub>Sb</sub>) for the S-rich film which also acts as carrier traps/ recombination sites, the Fermi level pinning effects lessen and hence improved V<sub>OC</sub> can be expected. Hence, investigating the S-rich  $Sb_2S_3$  film for the next efficiency breakthrough is worthwhile. However, even with the preferred [hk1] crystalline orientation in  $Sb_2S_3$ , which could benefit carrier transport, Sb<sub>2</sub>S<sub>3</sub> has low carrier mobility due to high bulk resistance and poor carrier collection efficiency. Furthermore, more research should be focused on designing a built-in electric field with a fully depleted absorber layer to alleviate the constraints of fill factor and carrier collection efficiency of Sb<sub>2</sub>S<sub>3</sub> solar cells caused by low carrier mobility. As a result, a p-i-n planar or sensitized structure with a fully depleted absorber, allowing the built-in electric field to be applied to the entire absorber layer, would result in increased carrier transport efficiency and, as a result, increased power conversion efficiency. The major energy loss process in  $Sb_2S_3$  has been attributed to the low charge carrier mobility due to the intrinsically self-trapping of photoexcited carriers in Sb<sub>2</sub>S<sub>3</sub> by lattice deformation, as demonstrated by (Yang et al. 2019; Grad et al. 2021). The "self-trapping phenomenon" in soft-1D  $Sb_2S_3$  materials is unavoidable, but it can only be minimized by stiffening the elastic properties of  $Sb_2S_3$  to increase the PCE of  $Sb_2S_3$  solar devices. As a result, it is critical to look for novel ways to overcome the self-trapping phenomenon in  $Sb_2S_3$  materials in order to break through the current PCE limits.

According to the simulation results, the major defects in  $Sb_2S_3$  are the limiting factor for device performance. The simulation of PCE and series/shunt resistance of  $Sb_2S_3$ 

film, on the other hand, revealed improved FF under optimized series/shunt resistance, implying that more efforts should be made to optimize Rs and Rsh to overcome the efficiency barrier. Poor series and shunt resistances have been found to arise as a result of non-ideal band alignment, the formation of Schottky contacts, element diffusion, and the formation of defects at the semiconductor/metal contact, so these parameters should be considered when optimizing Sb<sub>2</sub>S<sub>3</sub> solar cell performance. Another factor one should pay attention is the proper selection of ETL and HTL, as simulation results indicated that an efficient carrier transfer process could be achieved for  $Sb_2S_3$  with an ETL with a conduction band minimum of -4.4 eV < CBM < -3.2 eV and an HTL with a valence band maximum of -5.2 eV > VBM > -6.4 eV owing to the interfacial potential barrier become negligible with appropriate energy levels of both ETL and HTL. By exploring the effect of the relative positions of the CBM<sub>ETL</sub> vs. the work function of the front electrode as well as  $VBM_{HTL}$  Vs. the work function of the back contact, a PCE of 15.62% (Voc = 1.125 V,  $Jsc = 17.83 \text{ mA/cm}^2$ , FF = 77.91%) has been projected when the CBM<sub>FTI</sub> is -3.4 eV,  $\Delta E_{C-F}$  is -0.3 eV, VBM<sub>HTL</sub> L is -6 eV and  $\Delta E_{V-B}$  is -0.1 eV. As it has been suggested the best PCE of the  $Sb_2S_3$  cell with the  $CBM_{ETL}$  and  $VBM_{HTL}$  at -3.5 eV and -6.1 eV respectively, it is worthy to investigate different suitable ETL and HTL in order to break the efficiency barrier. For an average Sb<sub>2</sub>S<sub>3</sub> thickness of 0.8 µm, the highest device performance has been predicted at lower values of Nt ( $10^{15}$  cm<sup>-3</sup>) and larger values of  $L_{\rm D}$  (1.6 µm). On the other hand, it has been demonstrated that hetero-junction quality can improve device performance by maintaining a lower interface defect density of ~10<sup>9</sup> cm<sup>-2</sup> at both ZnS/  $Sb_2S_3$  and  $Sb_2S_3/Cu_2O$  interfaces. On the other hand, it has been demonstrated the difficulty of conductivity increase through external p-type doping in intrinsic Sb<sub>2</sub>S<sub>3</sub> as it may lead to producing more donor V<sub>S</sub> sites, consequently producing many electron carriers and pushing the Fermi level up, and thus make the p-type doping difficult to be realized by external doping. Hence, as suggested by Cai et al., attempts should be done to increase the p-type doping by a two-step doping strategy (Cai et al. 2020). Hence a proper experiment should be carried out to increase the p-type conductivity by passivating the  $Sb_2S_3$  Vs defects first by using O under the S-rich condition to increase the hole carrier concentration and suppress the other p-type limiting and recombination-center donor defects, and later by introducing different external p-type dopants such as Pb, to further increase its p-type conductivity to overcome the current efficiency bottleneck of  $Sb_2S_3$ -based solar cells.

Finally, given the recent interest in the theoretical and experimental investigation of excited-state carrier dynamics and defect properties in  $Sb_2S_3$ , concerted optimization of  $Sb_2S_3$  based solar cell based on theoretically predicted parameters may lead to a better understanding of the different recombination losses in both  $Sb_2S_3$  bulk and interfaces of  $Sb_2S_3/ETL$  an  $Sb_2S_3/HTL$  could lead to promoting device performance (Cai et al. 2020; Courel et al. 2019; Cao et al. 2020; Xiao et al. 2020; Islam and Thakur 2020; Yang et al. 2019; Grad et al. 2021; Lian et al. 2021; Li et al. 2021).

## 5 Conclusion

Despite reported higher efficiencies for sensitized  $Sb_2S_3$  Solar cells, the planar device structure is more competitive for  $Sb_2S_3$ -based solar cells. The high density of interface defects and poor carrier transport are the limitation of  $Sb_2S_3$  based solar cells. The major defects  $V_{sb}$  and  $V_s$  in  $Sb_2S_3$  can be mitigated by doping with Zn/Cu and Br/Cl leading to increase charge carrier density and electron transport properties. A proper selection of the

buffer layer is important for efficient charge collection and to reduce the charge recombination. The major energy loss process in  $\text{Sb}_2\text{S}_3$  is due to the "self-trapping phenomenon" in soft-1D  $\text{Sb}_2\text{S}_3$  caused by lattice deformation, which cannot be totally unavoidable but can only be minimized by stiffening the elastic properties of  $\text{Sb}_2\text{S}_3$ . Hence, it is critical to look for novel ways to overcome the self-trapping phenomenon in  $\text{Sb}_2\text{S}_3$  materials in order to break through the current PCE limits. This review could lead to the utilization of earthabundant and harmless  $\text{Sb}_2\text{S}_3$  in the future.

Authors' contribution JB contributed to the study conception and design. Material preparation, data collection and analysis were performed by MAF, AM, HT, C-FY and JB. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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### Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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