Current status of n-type SnS: paving the way for SnS homojunction solar cells

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Abstract
Orthorhombic SnS is a promising thin-film solar-cell material composed of safe and abundant elements with suitable optical properties for photovoltaic application. For approximately two decades, SnS solar cells have employed heterojunction structures with p-type SnS and other n-type semiconductors because undoped SnS typically exhibits p-type electrical conduction. However, their conversion efficiency has remained stagnant at 4%–5% for a long time. A breakthrough is required to significantly improve their conversion efficiencies before SnS solar cells can be put into practical use. Therefore, this comprehensive review article establishes the current state of the art in SnS solar cells, with an aim to accelerate both fundamental research and practical applications in this field. We discuss issues specific to SnS heterojunction solar cells, the advantages of the homojunction structure, and summarize recent advances in the n-type conversion of SnS by impurity doping, which is required to form a homojunction. The latter half of this article describes the latest research on the fabrication of n-type single crystals and films of halogen-doped n-type SnS, which is prepared via a doping system suitable for practical use. We conclude the article by summarizing the current status and future work on SnS homojunction devices, including the development of high-efficiency multi-junction SnS solar cells by band gap engineering.

1. Introduction

Compound semiconductors with high optical absorption coefficients of over $10^4$ cm$^{-1}$ near the band edge can absorb more than 99% of sunlight, even in thin-film form with a thickness of 2–3 µm. Thin-film solar cells using such semiconductors are typically much cheaper than crystalline Si solar cells, which require a thickness of ~200 µm, as they can be manufactured using fewer raw materials. In addition, the thinness of these solar panels makes them lightweight, allowing them to be installed in a broader range of locations, including low-load-resistant building roofs or walls. Renewable energy is extremely important for realizing a carbon-neutral society, and the development and widespread use of inexpensive and lightweight thin-film solar cells is therefore important. Compound thin-film solar cells containing Cu(InGa)Se$_2$ (CIGS) and CdTe absorber layers exhibit practical conversion efficiency and are commercially available; however, their widespread use is hampered by the requirement for expensive or rare (In, Ga, and Te) and toxic (Cd) elements. New, safer, thin-film solar-cell materials composed of abundant, and therefore inexpensive, elements, are required to meet the global power demand and to significantly increase the use of thin-film solar cells.

SnS is one of the three compounds in the Sn–S binary system, along with Sn$_2$S$_3$ and SnS$_2$ [1, 2]. SnS adopts either an orthorhombic structure (α-SnS, space group: Pnma) [3] or a more recently-discovered cubic structure (π-SnS, space group: P2$_1$3) [4]. The term ‘SnS’ in this review denotes the conventional α-SnS, in which Sn–S layers are stacked along the a-axis direction (figure 1(a)). Although α-SnS is an indirect semiconductor, it possesses a direct band gap (~1.3 eV), with a slightly higher energy than the
indirect band gap (\(\sim 1.1\) eV), and exhibits a high optical absorption coefficient of over \(10^4\) cm\(^{-1}\) at the band edge (figure 1(b)) \([5]\). Because SnS is composed of non-toxic and abundant elements \([6]\), SnS solar cells are expected to be safe and inexpensive energy sources. Figure 1(c) shows the estimated material costs of the absorber layers required to fabricate a 1 GW module (left axis) and the number of possible 1 GW modules that can be manufactured based on the estimated global reserves of the most limiting element (right axis), assuming a 20\% conversion efficiency \([7]\). The material costs required for SnS solar cells are approximately 1/14 and 1/2 of those of CIGS and CdTe solar cells, respectively. The constituent elements of SnS, Sn and S, are so abundant that 100 times more solar modules can be produced from SnS than from CIGS or CdTe. Unlike other absorber materials such as Cu\(_2\)ZnSnS\(_4\) (CZTS) and CuSbS\(_2\) (CAS), SnS is a simple binary compound; thus, its composition in thin-films can be more easily controlled using physical-vapor and liquid-phase techniques.

Owing to these advantages, the use of SnS as a light absorber for thin-film solar cells has been studied for approximately two decades. SnS intrinsically exhibits p-type electrical conduction, while n-type electrical conduction was not reported in SnS for a long time. Conventional SnS solar cells have therefore employed a heterojunction structure between thin films of p-type SnS and other n-type semiconductors such as CdS. The evolution of the conversion efficiency of heterojunction solar cells with an SnS absorber is plotted in figure 1(d), while the number of publications related to SnS solar cells is also plotted as an indicator of SnS research activity. Research on SnS heterojunction solar cells started around the year 2000. By approximately 2012, the conversion efficiency of SnS-containing solar cells improved following an increase in research activity, as evidenced by the number of related publications. From 2013–2015, the fabrication of SnS thin films was achieved by numerous techniques, including pulsed laser deposition (PLD) \([8]\), sputtering \([9, 10]\), chemical vapor deposition \([11]\), evaporation \([12, 13]\), and liquid–phase synthesis \([14]\). Concurrently, the conversion efficiency of SnS thin-film solar cells increased to approximately 4\% \([15]\). However, after Gordon et al achieved a conversion efficiency of 4.4\% in 2014, the maximum conversion efficiency remained unchanged for 5 years, being only slightly improved to 4.8\% in 2019 \([16]\). In contrast, the conversion efficiency of CIGS solar cells improved from 5\% in 1976 to 12\% in five years \([17]\). The number of studies related to SnS solar cells slowly declined as the conversion efficiency stagnated; thus, a breakthrough is clearly
essential to substantially improve the conversion efficiency of SnS solar cells, which will certainly invigorate research into the fundamental research and practical applications of SnS solar cells.

This review concentrates on n-type SnS, which is essential in the construction of homojunction SnS solar cells. We expect that this detailed overview will encourage further research to improve the conversion efficiency of SnS solar cells. In section 2, we discuss the factors that hinder the improvement of the conversion efficiency in SnS heterojunction solar cells and the necessity of developing a homojunction structure to overcome these issues. Section 3 introduces the doping techniques used for the carrier conversion of the intrinsically p-type SnS into n-type SnS. Section 4 discusses halogen-doped SnS, which is prepared using a doping system suitable for photovoltaic applications, including fabrication techniques for single crystals and thin films. In section 5, we discuss the characteristics of prototype homojunction solar cells containing single-crystalline n-type SnS and the expected future work. In sections 6 and 7, we provide a discussion of the future direction of research into n-type SnS and conclude this review.

2. Problems specific to the SnS heterojunction and advantages of homojunction

Table 1 summarizes the photovoltaic characteristics of representative SnS heterojunction solar cells. Characteristics of the CdTe and CIGS cells in the early stages of their development are also shown for reference. Various n-type semiconductors are used as the n-type layer of SnS heterojunction devices, including Cds, which is the most common n-type layer in CIGS and CdTe solar cells. The short-circuit current densities (JSC) of SnS heterojunction devices are comparable to those of early-stage CdTe and CIGS solar cells; however, their open-circuit voltages (VOC) are much lower than those of the latter. The theoretical limit of VOC is linearly dependent on the band gap of the absorber (figure 2). Considering that the fundamental band gap of SnS is -1.1 eV, a VOC in the range of 700–800 mV is expected; however, the experimentally measured VOC of SnS heterojunction cells is significantly lower than the expected value (300–400 mV). As the JSC values of SnS heterojunction devices are comparable to those of early-stage CdTe and CIGS cells, the first and most significant barrier to SnS solar cells with high conversion efficiency is the low VOC. Two models have been proposed to explain the low VOC values of SnS heterojunction solar cells.

2.1. Unfavorable conduction band offset (CBO)

Figure 3(a) shows the ideal band alignment for a p–n heterojunction solar cell in which the p-type semiconductor is an absorbing layer. The CBO has a significant impact on the photovoltaic performance of cells with a p-type absorbing layer. To obtain a high VOC, a type-I alignment is preferred. In particular, a preferred CBO is ranging from 0 to +0.4 eV, where the conduction band energy of the n-type layer is preferably equal to or slightly higher than that of the p-type layer [30]. Such favorable conduction band alignment is realized at the heterojunction of CdTe or CIGS with n-type Cds, which results in high VOC (e.g. CBOs of CuIn0.5Ga0.5Se2/CdS and CdTe/CdS junctions are +0.2 [31] and +0.1–0.3 eV [32], respectively). Conversely, because the conduction band of SnS has a higher energy than that of Cds, the interface between p-type SnS and n-type Cds results in a type-II band alignment with a negative CBO and a cliff (figure 3(b)) [33–35]. Owing to this band alignment, recombination of the holes and electrons, which are the respective major carriers in p-type SnS and n-type Cds, is more likely to occur at the interface, thereby resulting in a lower VOC [36]. Such a band alignment arises from the intrinsic electronic structure of SnS, whose conduction band energy is ~0.5 eV higher than that of CdTe [34, 37]. Accordingly, it may be difficult to realize a heterojunction between p-type SnS and n-type Cds with a high VOC. To achieve a type-I band alignment with a high expected VOC, heterojunctions with n-type semiconductors possessing higher conduction band energies than that of Cds have been investigated, including Zn(O,S), Zn(O,S)N, and Zn1−xMg,xO (table 1). These n-type layers should result in a CBO in the ideal range (0 to +0.4 eV) [9, 11, 24, 38]; however, the maximum observed VOC is only ~400 mV, which represents a slight improvement over n-type Cds (VOC = ~300 mV), but is only approximately half of the expected VOC. The low VOC of SnS heterojunction solar cells may also arise from Fermi level pinning at the interface, as explained in section 2.2.

2.2. Fermi level pinning in p-type SnS

Klein et al reported in 2014 that the Fermi energy of p-type SnS thin film changes only by ~0.2 eV at the p–n heterojunction interface with various n-type semiconductor thin films such as ZnO or Cds (figure 4) [10]. This result suggests that the energy range over which the Fermi level of p-type SnS can be tuned at the interface is strongly limited by Fermi level pinning. Photovoltages in solar cells involving a p–n junction arise from quasi-Fermi level splitting. Therefore, if the tunable energy range of the Fermi level of the absorber is limited, a high VOC cannot be generated [39, 40]. This Fermi level pinning is one of the reasons that SnS heterojunction cells have a low VOC, although its origin has not been identified; it may arise from a bulk defect in the SnS or an interfacial defect.
Table 1. Photovoltaic characteristics of representative SnS heterojunction solar cells. The characteristics of CdTe and CIGS solar cells in the early stages of development are also shown at the bottom for reference.

| Cell structure | \( \eta \) (%) | \( V_{OC} \) (mV) | \( J_{SC} \) (mA cm\(^{-2}\)) | FF (%) | Year (reference) |
|----------------|----------------|-------------------|-----------------------------|--------|-----------------|
| SnO\(_2\)/p-SnS/CdS/ITO | 1.3 | 260 | 9.6 | 53 | 2006 [19] |
| Mo/p-SnS/Zn(O,S)/ZnO/ITO | 2.04 | 244 | 19.4 | 43.0 | 2013 [11] |
| Cu/p-SnS/Zn\(_{1-x}\)Mg\(_x\)O/ITO | 2.1 | 270 | 12.1 | 64 | 2013 [9] |
| Mo/p-SnS/(Sn,Ge)O\(_2\)/ZnO/ITO | 2.21 | 400 | 12.2 | 46 | 2019 [20] |
| Mo/p-SnS/Zn(O,S)/ZnO/ITO | 2.9 | 261 | 24.9 | 44.4 | 2014 [21] |
| P3HT/p-SnS/TiO\(_2\)/FTO | 3.0 | 313 | 24.8 | 39 | 2018 [22] |
| Mo/p-SnS/(Zn,Cd)S/ZnO/AZO | 3.72 | 405 | 22.9 | 40.1 | 2020 [23] |
| Mo/p-SnS/Zn(O,S):N/ZnO/ITO | 3.88 | 334 | 20.6 | 56.3 | 2014 [12] |
| Mo/p-SnS/SnO\(_2\)/SnO:ZnO/n-ZnO/ITO | 4.36 | 372 | 20.2 | 58 | 2014 [24] |
| Au/p-SnS/TiO\(_2\)/FTO | 4.8 | 330 | 24.7 | 58.5 | 2019 [16] |
| CdTe solar cells | 10 | 760 | 20 | 67 | [25] |
| CIGS solar cells | 17 | 650 | 33 | 77 | [25] |

Figure 2. Open-circuit voltages (\( V_{OC} \)) of solar cells containing various absorbers with record conversion efficiencies as a function of fundamental band gap. The theoretical S–Q limit line was taken from [26] and data points from [27, 28]. The Cu(In,Ga)(S,Se)\(_2\) (CIGSSe) absorber possesses a gradient band gap of 1.1–1.7 eV [29].

Figure 3. Schematic diagram of band alignment at the p–n junction of (a) an ideal heterojunction (e.g. between p-type CIGS or CdTe absorber and n-type CdS), (b) a p-SnS/n-CdS heterojunction and (c) an SnS homojunction. All values are in eV.

The p–n homojunction is composed of interfaces between the same materials with different Fermi energies (i.e. p- and n-type conductors). Thus, the crystal structure, band gap, and conduction/valence band energies of both layers are identical. In such junctions, the difference in the Fermi energies of the p- and n-layers induces band bending at the interface, resulting in a smooth band structure without discontinuities (figure 3(c)), thereby making interfacial recombination easier to prevent (section 2.1). In addition, the absence of lattice mismatch and the reduction in the number of dangling bonds at the heterojunction facilitate the formation of high-quality interfaces without a pinning level.
SnS homojunctions can therefore solve both the problems of an unfavorable CBO and Fermi level pinning at the interface in SnS heterojunction solar cells. Implementing a homojunction structure is a promising solution to improve the $V_{OC}$ of SnS solar cells. To achieve p–n homojunctions in SnS, carrier-type conversion of the intrinsically p-type SnS into n-type SnS is required.

3. Carrier-type conversion of p-type SnS to n-type by impurity doping

Figure 5(a) shows the formation enthalpy of various intrinsic defects in SnS as a function of the Fermi energy, calculated by Malone et al [41]. In the S-rich condition, the formation enthalpy of a Sn vacancy ($V_{Sn}$), which works as the acceptor, is very low and even negative with a Fermi energy above $\sim$0.7 eV, which lowers the Fermi energy (i.e. increases the hole concentration), thereby leading to p-type conduction in SnS. In the Sn-rich condition, $V_{Sn}$ acts as an acceptor with a low formation enthalpy, also resulting in p-type conduction. However, as S vacancy ($V_{S}$) and Sn-on-S antisite (SnS) act as donors with low Fermi energy, the hole concentration is thought to be lower under Sn-rich condition than that under S-rich condition. The calculated formation enthalpies of $V_{S}$ and SnS and the transition levels of these defects reported in the literature vary significantly owing to their sensitivity to the supercell size and the corresponding functional used in the calculations [8, 42, 43]. Nevertheless, the calculations in the literature confirm that SnS readily acts as a p-type conductor without intentional doping, which is consistent with experimental observations that existing undoped SnS always exhibits p-type conduction. Therefore, intentional impurity doping to compensate holes and generate electrons is required to convert the SnS from a p-type to an n-type semiconductor.

3.1. Cation doping

The most common method of carrier-type conversion in semiconductors involves impurity doping with cations having different valence states (aliovalent cation doping). For instance, doping the group-IV and group-II elements Si and Zn into GaAs generate electrons (n-type doping) and holes (p-type doping), respectively. Since SnS contains Sn$^{2+}$ cations, Bi$^{3+}$ and Sb$^{3+}$ are sensible candidates for aliovalent cation doping to achieve n-type conversion. Notably, doping of Bi$^{3+}$ and Sb$^{3+}$ into SnSe effectively results in n-type electrical conduction [44, 45]. To date, several research groups have attempted to achieve the n-type conversion of SnS by Sb doping. Sb incorporates into the Sn sites as Sb$$_{Sn}$ and compensates holes, making the SnS less p-type [46, 47]; however, n-type conduction was not obtained [46, 48, 49]. First-principles calculations also show that Sb doping reduces the hole concentration but does not result in n-type conduction [43], which is in good agreement with experimental observations. It has also been observed experimentally that Bi-doped SnS does not exhibit n-type conduction [50, 51], which is consistent with the high formation enthalpy of donor-type Bi$$_{Sn}$ predicted by first-principles calculations [43]. To date, there have been no experimental reports describing the successful n-type conversion of SnS via aliovalent cation doping.

In 2015, Ran et al developed an interesting and unique doping technique to achieve n-type conduction in SnS, and demonstrated that Sn$_{1-x}$Pb$_x$S thin films in which SnS was doped with isovalent Pb$^{2+}$ ions exhibited n-type conduction [50]. In Sn$_{1-x}$Pb$_x$S, the interlayer distance becomes wider than that in SnS because Pb$^{2+}$ has a larger ionic radius than Sn$^{2+}$. Such geometrical alteration lowers the formation enthalpy of donor-type defects (Sn$_{c}$ and Pb$_{a}$), thereby generating electrons and resulting in n-type conduction [43, 50]. This mechanism is named 'geometrical doping', and was reported to achieve n-type conduction with a carrier concentration of $10^{12}$–$10^{15}$ cm$^{-3}$ at a Pb concentration of 0.2 $< x < 0.5$ (figure 5(a)). This concentration of Pb impurities is extremely high compared to that achieved via the typical impurity doping technique and therefore, Sn$_{1-x}$Pb$_x$S is considered as a solid solution of SnS and PbS rather than a doped material. Furthermore, the lattice constants of Sn$_{1-x}$Pb$_x$S vary linearly between those of SnS and PbS in accordance with Vegard’s law; for instance, the $a$-, $b$-, and $c$-axis lattice constants of Sn$_{0.5}$Pb$_{0.5}$S are $+1.8\%$, $+2.7\%$, and $−1.6\%$, respectively, relative to those of undoped SnS. The band gap increases with increasing level of PbS.

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**Figure 4.** Schematic diagram of Fermi level pinning of SnS at the interface with n-type semiconductors.
alloying, i.e. it is ∼0.1 eV larger in Sn$_{0.5}$Pb$_{0.5}$S than in SnS [50]. Following this report, several studies investigated the thermoelectric conversion performance of n-type Sn$_{1−x}$Pb$_x$S [52]; however, n-type Sn$_{1−x}$Pb$_x$S has not been studied as an absorber layer for solar cells, probably owing to the presence of the toxic Pb or a low carrier concentration that give it insulating properties.

3.2. Anion doping

In 2016, Yanagi et al first demonstrated n-type conduction in SnS sintered pellets by halogen-doping, in which the anion S$^2-$ was substituted with the halogen, Cl$^-$ [53, 54]. n-type conduction is observed in SnS$_{1−x}$Cl$_x$ with $x > 0.0025$ (figure 6(b)). First-principles calculations also indicate that Cl is incorporated into the S site as Cl$_S$ and generates electrons over a wide range of compositions (figure 5(b)), which is consistent with the experimental results; thus, doping with Cl is a promising n-type conversion strategy. Doping with another halogen, Br, is also known to induce n-type conduction in SnS [55].

Halogen-doped n-type SnS does not contain highly toxic elements. In addition, by adjusting the dopant concentration (0.0025 < $x$ < 0.005 for SnS$_{1−x}$Cl$_x$ sintered ceramics), the carrier concentration can be controlled over a wide range of $10^{15}$−$10^{18}$ cm$^{-3}$. Moreover, halogen doping does not affect the lattice constant; thus, no lattice mismatch occurs in a homojunction with undoped SnS [56]. Given these advantages, halogen-doped n-type SnS has attracted considerable attention as a practical doping system capable of forming high-quality homojunctions, thus triggering a number of subsequent studies. In section 4, we introduce the trends and future directions in research into halogen-doped n-type SnS, such as the fabrication and physical properties of single crystals and thin films.
4. Halogen-doped n-type SnS

4.1. n-type SnS single crystals

Halogen-doped n-type SnS was first reported in sintered polycrystalline ceramic form (section 3.2). Single-crystalline halogen-doped n-type SnS was then reported by Iguchi et al., who synthesized a Cl-doped SnS single crystal by the flux method using an SnCl$_2$ self-flux [50]. In this case, the maximum single-crystal size was approximately 3 mm × 7 mm. Following this work, Kawanishi et al. grew centimeter-sized Cl- and Br-doped single crystals via the flux method using metallic Sn as the flux (figure 7) [2].

The halogen-doped SnS single crystals prepared by both of the above flux methods contained Cl- or Br-dopant concentrations of approximately 0.1–0.2 atom% (corresponding to ~2–4 × 10$^{19}$ cm$^{-3}$). Their carrier concentrations and mobilities were both of the order of 10$^{17}$ cm$^{-3}$ and 100–300 cm$^2$ V$^{-1}$ s$^{-1}$, respectively (figure 8). A halogen-doped n-type SnS single crystal was used as the n-type substrate of the prototype homojunction solar cells (section 5). When applying to the photovoltaic devices, both the dopant and carrier concentrations are preferably reduced to increase the width of the space charge region and minority carrier diffusion length in n-type single crystals. The development of a synthetic route to single crystals in which these properties can be controlled should also be a goal of future studies.

The layered structure of SnS (figure 1(a)) facilitates cleavage of the single crystal and preparation of a clean surface. Therefore, photoelectron spectroscopy can be performed on samples with clean surfaces simply by prior cleavage in a vacuum without resorting to costly in-situ experiments [2, 57]. Figure 7(d) shows the Fermi energy positions and work functions of the SnS single crystals determined by x-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy [2]. The Fermi levels of n-type SnS...
single crystals were 0.4 eV higher than that of the undoped p-type SnS and very close to the conduction band minimum. This is consistent with the experimental observation that n-type SnS single crystals exhibited little temperature-dependence on carrier concentration and were almost degenerated semiconductors [2, 56].

4.2. n-type SnS thin films
The Cl-doped n-type SnS thin films were firstly deposited in 2021 by Suzuki et al. (figure 9(a)) [58], who demonstrated that n-type conduction is achieved in SnS thin films by the concurrent introduction of a Cl dopant and a sulfur plasma supply (figure 9(b)). SnS thin film deposited without a sulfur plasma supply did not exhibit n-type conduction, despite the presence of similar Cl dopant concentrations. The necessity of a sulfur plasma supply to generate n-type conduction in SnS is explained as follows: SnS exhibits p-type conduction by forming acceptor-type defects under both S-rich and Sn-rich conditions (figure 5(a)). In an open vacuum system for thin-film fabrication, such as evaporation, sputtering, and PLD, sulfur is easily lost during processes owing to its high vapor pressure. Notably, the absorption spectra of thin films deposited without sulfur plasma supply show a broad absorption peak at 0.9–1.3 eV (figure 9(c)), which is presumably due to sulfur deficiency. This defect likely prevents n-type conversion of SnS. These results indicate that halogen doping and prevention of sulfur deficiency (achieved via the supply of sulfur plasma in Suzuki et al’s study) are both important for obtaining n-type conduction. First-principles calculations indicate that Sn-rich (S-poor) SnS is more favorable for n-type conduction (figures 5(a) and (b)); however, this experiment demonstrates that an excess of Sn does not necessarily ensure n-type conduction. Suzuki’s study demonstrated a process wherein n-type conduction is realized in halogen-doped SnS thin films via the supply of a highly reactive sulfur source. Similarly, the supply of highly reactive sulfur during other thin-film deposition methods, such as evaporation and PLD, may also lead to efficient electron generation and n-type conduction.

The n-type SnS thin films obtained in Suzuki’s study exhibited a carrier concentration of $2–3 \times 10^{18}$ cm$^{-3}$, approximately one order of magnitude higher than that of n-type single crystals (figure 8). Moreover, the Cl-dopant concentration was 0.018 atom% ($3.7 \times 10^{18}$ cm$^{-3}$), indicating a very high dopant activation rate of ~60%. Such a high dopant activation rate is preferable to inhibit the introduction of excessive dopants, thereby decreasing the recombination center, and also to allow the carrier concentration to be controlled by adjusting the dopant concentration.

The morphology of p-type SnS thin films is well known to be strongly affected by the sputtering conditions, including the sputtering pressure and substrate temperature, to a greater extent than other compound semiconductors. The crystallite sizes and shapes (e.g. spherical, needle-like, or flake-like) vary significantly depending on the conditions [59, 60]. Determining the optimal sputtering conditions is therefore important to ensure high-quality interfaces are established during the formation of homojunctions. The minority carrier diffusion length of SnS thin films should also be analyzed because the appropriate layer thickness is determined based on the minority carrier diffusion length to ensure efficient carrier collection. It should be noted here that the optimal layer thickness was discussed in terms of the assumed minority carrier diffusion length through the homojunction with an SnS single crystal [61].
5. Prototype homojunction solar cells with n-type SnS single crystals

In 2020, Kawanishi et al predicted the potential of SnS homojunction solar cells using prototype homojunction solar cells incorporating n-type SnS single crystals [61]. In this prototype, an undoped p-type SnS thin film was deposited on a single-crystalline n-type SnS substrate (figure 10(a)). The J–V characteristics of this prototype homojunction cell exhibited a $V_{OC}$ of 360 mV (figure 10(b)), which is lower than the observed highest $V_{OC}$ of the heterojunction cells ($V_{OC} = 405$ mV, table 1). This low $V_{OC}$ is primarily caused by the large reverse saturation current density of the device ($J_0 = 3.6 \times 10^{-3}$ mA cm$^{-2}$). In other words, charge carrier recombination through defects around the interface resulted in a low $V_{OC}$, indicating that simply forming a homojunction does not necessarily ensure a high $V_{OC}$. However, a built-in potential ($V_{bi}$) of 0.92 V was determined by capacitance measurements [61], which is much larger than those of the heterojunctions ($V_{bi} \sim 0.7$ V [19, 70]). Considering that the available $V_{OC}$ is $\sim 0.1$ eV lower than $V_{bi}$, it was experimentally demonstrated that a high $V_{OC}$ can be obtained using homojunction solar cells. The low $V_{OC}$ (i.e. the large reverse saturation current density) of this prototype device is thought to arise from the presence of an oxidation layer at the interface formed by the cleavage of a single crystal in air prior to the formation of the interface. Alternatively, impurities in the p-type SnS layer from residual impurity gas in the deposition chamber may explain the low $V_{OC}$. Moreover, the number of defects at the interface of SnS heterojunction thin-film solar cells can be reduced by a post-annealing process [71, 72], which is very likely to also be effective to homojunction solar cells. Assuming that interface defects can be reduced by these means, solar cells with this structure are expected to exhibit a much higher $V_{OC}$ and conversion efficiency.

The formation of ideal homojunctions with fewer interfacial defects may be facilitated by using the cleaved surface of the single crystal as a substrate in either the n- or p-layer rather than by using thin films in both layers as the latter would require appropriate deposition substrates. Solar cells employing the cleaved surface of single-crystalline SnS are excellent platforms to investigate the properties of ideal homojunctions, demonstrate the high potential of SnS as a solar-cell material, and identify key factors influencing photovoltaic properties. These results form a ‘benchmark’ for SnS solar cells and provide important insights for improving conversion efficiency, which may facilitate improvements in the fabrication process of SnS thin films and homojunction thin-film cells.

6. Future work

A Fermi level shift due to doping was observed on the cleaved surface of an SnS single crystal (figure 7). In contrast, doped semiconductors often do not exhibit a Fermi level shift at the surface owing to Fermi level pinning induced by the surface state (e.g. the energy difference between the Fermi level of p-type and n-type doped Si surfaces is less than 0.1 eV [73]). The Fermi level shift observed in the cleaved SnS surface indicates that there is no such surface state that induces Fermi level pinning, probably because the cleavage surface of
SnS is a van der Waals surface without dangling bonds, which enable the analysis of the intrinsic electronic state of the surface. In addition, the van der Waals surfaces (i.e. the cleavage surfaces) of MoS$_2$ and WSe$_2$, which have a layered structure similar to that of SnS, are less likely to exhibit Fermi level pinning even at the interface with other semiconductors \[74\]. The cleavage surface of SnS will therefore facilitate the study of the electronic structure at the interfaces (i.e. band alignment) between SnS and other semiconductors, and can also be used to construct ideal homojunction interfaces.

High-efficiency solar cells with multi-junctions exhibiting a significantly higher conversion efficiency than single-junction solar cells have recently emerged \[27\]. The band gap tunability is important for SnS to be applied to multi-junction solar cells. Figure 11 shows the band gap variation of the solid solutions of SnS with related compounds. The band gap of SnS can be tuned in the range of 0.9–1.6 eV by forming alloys with SnSe or GeS. It may also be possible to control the band gap by preparing a solid solution of SnS with other chalcogenides. Future work should investigate the carrier-type control and homojunctions of such solid solutions to improve the conversion of multi-junction devices.

Although this review has primarily discussed orthorhombic $\alpha$-SnS, solar cells with cubic $\pi$-SnS, which has a band gap of 1.7 eV \[77–79\], is also being investigated, with a crystal structure being reported as recently as 2015 \[4\]. The band gap of the semiconductor alloy, $\pi$-Sn(S,Se), can be adjusted in the range of 1.4–1.7 eV by altering the composition \[80\], while it is also has advantages in multijunction applications, as shown in figure 11. Like undoped $\alpha$-SnS, $\pi$-SnS exhibits p-type electrical conduction; thus, n-type doping to enable the formation of $\pi$-SnS heterojunctions may be another interesting future direction of research in this field.

Binary Sn–S compounds other than SnS include the n-type semiconductors SnS$_2$ and Sn$_2$S$_3$, which have band gaps of $\sim$2 and $\sim$1 eV, respectively. SnS$_2$ and Sn$_2$S$_3$ are often formed as undesired and troublesome impurity phases during the fabrication of SnS thin films, in which they can inhibit carrier transport \[81, 82\]. Conversely, several studies have utilized the n-type nature of these materials to form heterojunction solar cells with p-type SnS. Since the band gap of Sn$_2$S$_3$ ($\sim$1 eV) is favorable for single-junction solar cells, theoretical studies of the p-type doping of Sn$_2$S$_3$ have been conducted to investigate the possibility of forming Sn$_2$S$_3$ homojunctions \[42\]. The further development of solar cells using such Sn-S compounds also requires the development of improves deposition processes that enable the formation of pure single phases without any secondary phases.

SnS is also expected to be an excellent thermoelectric conversion material \[83, 84\]; however, a full discussion of this concept is outside the scope of this review. In particular, n-type SnS is predicted to have a higher thermoelectric conversion performance than p-type SnS based on first-principles calculations \[85\], and several experimental studies on this concept have been reported \[55, 86\]. Achieving high thermoelectric performance in n-type SnS requires a high carrier concentration of the order of $10^{19}$ cm$^{-3}$. Unlike single-crystalline SnS, which has a low halogen dopant activation rate ($\sim$1%, section 4.1), Cl-doped n-type SnS thin films exhibit a high activation rate ($\sim$60%, section 4.2), which should be suitable for increasing the carrier concentration. Therefore, applying n-type SnS thin films to thermoelectric conversion materials is also worth investigating.
7. Conclusion

SnS is undoubtedly one of the most suitable thin-film solar-cell materials owing to its non-hazardous nature, the abundance of Sn and S, and its simple binary chemical composition that can be easily controlled during the synthesis process. In this review, we suggested that the realization of an n-type SnS homojunction structure can be a breakthrough that will improve the conversion efficiency of SnS solar cells, which has remained stagnant at 4%–5% for many years. Although SnS homojunction devices were once considered a far-fetched concept, the emergence of halogen-doped n-type SnS in 2016 changed the research landscape of this field. To date, several halogen-doped n-type single crystals and thin film have been reported, while prototype homojunction cells using n-type single crystals have been developed. We hope that further study of n-type SnS and homojunctions will significantly improve the conversion efficiency of SnS solar cells and thereby accelerate the development of practical applications for these materials.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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