Facile control over the morphology of phase pure tin monosulfide (SnS) thin films, a promising future absorber for thin film solar cells, is enabled by controlling the growth kinetics in vapor transport deposition of congruently evaporated SnS. The pressure during growth is found to be a key factor in modifying the final shape of the SnS grains. The optimized cube-like SnS shows p-type with the apparent carrier concentration of $\approx 10^{17} \text{ cm}^{-3}$ with an optical bandgap of 1.32 eV. The dense and flat surface morphology of 1 µm thick SnS combined with the minimization of pinholes directly leads to improved diode quality and increased shunt resistance of the SnS/CdS heterojunction (cell area of 0.30 cm$^2$). An open-circuit voltage of up to 0.3068 V is achieved, which is independently characterized at the Korea Institute of Energy Research (KIER). Detailed high-resolution transmission electron microscopy analysis confirms the absence of detrimental secondary phases such as Sn$_2$S$_3$ or SnS$_2$ in the SnS grains or at intergrain boundaries. The initial efficiency level of 98.5% is maintained even after six months of storage in air, and the final efficiency of the champion SnS/CdS cell, certified at the KIER, is 2.938% with an open-circuit voltage of 0.2912 V.

The ever-increasing demand for sustainable energy has motivated efforts to develop highly efficient thin film solar cells (TFSCs). The current leading TFSCs employ mainly Cn(In,Ga)$_{3}$ (CIGS) and CdTe absorbers with efficiencies of over 22%.[2,3] Owing to the scarcity of indium and the toxicity of cadmium, new absorbers composed of cheap, nontoxic, and earth-abundant elements have been investigated, and tin-based chalcogenides have been identified as promising candidates.[4] The most studied tin chalcogenide material is Cu$_2$ZnSn(S,Se)$_4$ (CZTS/Se), which has a record efficiency of 12.6%.[5] Further improvements in efficiency have been inhibited in recent times owing to a considerable deficiency of the open-circuit voltage ($V_{oc}$), which arises from cation disordering and severe interface recombination.[6,7]

Orthorhombic herzenbergite tin monosulfide (SnS, JCPDS No. 39-0354, $a = 4.3291 \text{ Å}$, $b = 11.1923 \text{ Å}$, $c = 3.9838 \text{ Å}$) is another emerging tin-based chalcogenide absorber;[8,9] it has a suitable direct bandgap of $\approx 1.3$ eV with a high optical absorption coefficient of $10^5 \text{ cm}^{-1}$ in the visible region of solar spectrum. The first meaningful report of orthorhombic SnS-based TFSCs was made by Reddy et al., using spray pyrolysis in 2006.[10] The SnS absorber coupled with In-doped CdS as an n-type buffer layer exhibited 1.3% efficiency. Since then, many research groups have devoted considerable effort toward developing highly efficient SnS-based TFSCs, but most of the reported efficiencies were less than 1%.[11–14] This low efficiency was mainly ascribed to the poor quality of the SnS absorbers, which contained secondary phases. The growth of SnS easily leads to the formation of secondary phases such as n-type Sn$_2$S$_3$, SnS$_2$,[15] which are detrimental to the cell efficiency.[16]

The current record efficiency of 4.36% among SnS TFSCs was reported by Sinsermsuksakul et al. in 2014, and featured three notable major modifications: (i) growth of the p-type SnS by modified atomic layer deposition (ALD) at 200 °C and successive annealing of the absorber at 450 °C in an H$_2$S environment, (ii) tuning of the conduction band offset (CBO) using an ALD-Zn(O,S):N buffer layer, and (iii) reduced interface recombination by the formation of a thin SnO$_2$ layer ($\approx 1$ nm) between the SnS and Zn(O,S):N.[17] Particularly, the insertion of the SnO$_2$ layer was the most critical factor to enhance the efficiency from its 2.50% baseline (without interfacial SnO$_2$) to 4.36%, mainly due to the increase of the $V_{oc}$ from 0.26 to 0.37 V.

The ever-increasing demand for sustainable energy has motivated efforts to develop highly efficient thin film solar cells (TFSCs).[1] The current leading TFSCs employ mainly Cn(In,Ga)$_{3}$ (CIGS) and CdTe absorbers, as an n-type buffer layer exhibited 1.3% efficiency. Since then, many research groups have devoted considerable effort toward developing highly efficient SnS-based TFSCs, but most of the reported efficiencies were less than 1%.[11–14] This low efficiency was mainly ascribed to the poor quality of the SnS absorbers, which contained secondary phases. The growth of SnS easily leads to the formation of secondary phases such as n-type Sn$_2$S$_3$, SnS$_2$,[15] which are detrimental to the cell efficiency.[16]

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In the same year, Steinmann et al. also reported an efficiency of 3.88% for thermally evaporated SnS TFSCs.[18] Purification of the SnS powder prior to the evaporation was found to contribute a reduction in the incorporation of secondary phases, and the three modifications mentioned above were also applied to achieve the near 4% efficiency. These two pioneering and collaborative works are the only reports of SnS-based TFSCs with an efficiency exceeding 3% until now.

Meanwhile, it is worth noting that metastable cubic SnS has also been highlighted as an emerging absorber.[19] Large optical bandgap of 1.7 eV and its isotropic nature are beneficial to obtain higher Voc compared to orthorhombic SnS.[20] Although the highest efficiency of 1.28% reported by Garcia-Angelmo et al.[21] is still lower than that of orthorhombic SnS TFSCs, it has a potential to be a viable alternative.

Coming back to orthorhombic SnS TFSCs, the relatively poor performance and reproducibility is mainly due to the great deficiency of their Voc.[22] The large variation in the band edge energy of orthorhombic SnS depending on its crystal orientation may account in part for such behavior.[23] The obtained Voc values are 0.37[18] and 0.33 V[18] for the above-mentioned 4.36% and 3.88% cells, respectively. For most of the orthorhombic SnS TFSCs, lower Voc values of less than 0.23 V are reported.[14,24–28] Notably, Minnam Reddy et al. reported a Voc of 0.575 V with a (Zn,Mg)O buffer layer, but the cell efficiency (2.02%) was less than 3% due to slightly poor short-circuit current density (Jsc) and fill factor (FF).[29] One of the problems, which is simple in concept but difficult to solve practically for SnS, is the poor quality of SnS and its increased shunt loss.[30]

Orthorhombic SnS is known to naturally form a strongly bound ribbon-like (plate-like) or layered structure.[31] The anisotropic nature of SnS often provides unique opportunities for optical or energy applications.[32] However, the high-temperature processes of film growth or postdeposition annealing, which are often used in the TFSC community to improve the crystalline quality of the absorbers, tend to form large amounts of pinholes in SnS. These lead to the low observed Voc values, most of which are less than 0.23 V, and in the worst case, to full shunting of the cell.[33] Unfortunately, the underlying mechanism of the successful growth of orthorhombic SnS with a dense morphology to achieve over 3% efficiency is not clear for either modified-ALD[17] or thermal evaporation.[18] Therefore, finding an accessible solution for the controlled growth of pinhole-free SnS absorbers, while maintaining high phase purity and adequate crystal quality, will be essential for continued academic interest in SnS TFSCs and for finally achieving an efficiency of greater than 5% in the near future.

In this study, we demonstrate a simple and facile way to modify the shape of vapor-transport-deposited (VTD) orthorhombic SnS grains from plate-like to more cube-like by controlling the growth kinetics. VTD is a proven, low-cost technique for the growth of commercial CdTe absorbers.[14] We note that Wangperawong et al. recently reported the growth of SnS, Sn2S3, and SnS2 by VTD,[34] however, only plate-shaped chalcogenides were formed, without any attempt at shape control. To inhibit the inherent growth of layered (or plate-shape) SnS, we intentionally increased the growth pressure during deposition using a flow of inert Ar gas. It was revealed that densely packed SnS film grows in kinetically limited conditions (optimized growth pressure of ≈1.4 Torr), while plate-like SnS prevails in low pressure conditions (i.e., ≈2 mTorr, without Ar flow). X-ray diffraction (XRD), Raman spectroscopy, and high-resolution transmission electron microscopy (HR-TEM) wereexploited to confirm that the grown cube-like SnS thin film has high crystallinity, without any detrimental secondary phases.

In addition, SnS/CdS heterojunction TFSCs were fabricated to investigate the impact of the SnS morphology. Although CdS has been reported to form an unfavorable band alignment with SnS, unlike CIGS or CZTSSe,[36] chemical-bath-deposited (CBD) CdS is a useful system compared to the relatively complex ALD-Zn(O,S),[37–39] to investigate the effect of the shape of the SnS on the device performance. It was demonstrated that the shape of the SnS grains directly determines the Voc values of the cells; a gradual increase in Voc was observed as the morphology changed from plate-like to cube-like SnS. In-depth TEM analysis of the phase purity of the SnS (intra- and inter-grains) along with the fabricated SnS/CdS TFSCs was also performed. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were used to determine the band alignment of the fabricated cells. Finally, the long-term stability of the efficiency of the champion cell was also monitored. The champion cell was stored in an air environment for six months, and little or no deterioration was observed (98.5% of the original efficiency). The certified efficiency of the champion cell after storage was 2.938%, which is the highest efficiency ever reported for an SnS-based TFSC with a CdS buffer layer.

Figure 1a,b shows the change in the morphology of the grown SnS depending on the growth pressure at a fixed furnace temperature of 600 °C (see the Experimental Section for details). At a low growth pressure of 2 mTorr during VTD, plate-like SnS grains with elongation in one direction were observed (Figure 1a). The growth followed the layered crystal structure of orthorhombic SnS, which is frequently observed in SnS growth by other methods due to the anisotropic growth rates of planes.[35,40] When the growth temperature was further increased to 700 °C, plate-shaped SnS with noticeably thinner plates aligned more perpendicularly to the substrate was obtained, while hardly any SnS growth occurred at 500 °C (Figure S1, Supporting Information). The open structure of Figure 1a with large pinholes was not considered to be suitable for TFSCs, as it would lead to poor shunt resistance of the cells. As discussed later, we experimentally confirmed this issue.

By contrast, densely packed and more cube-like grains formed as the growth pressure was gradually increased to 1.4 Torr, as shown in Figure 1b (Location (1) in Figure S2b, Supporting Information). The uniformity of the morphology over a large area was confirmed by the low-magnification plan-view scanning electron microscopy (SEM) image (Figure S3, Supporting Information). The corresponding cross-sectional SEM image in Figure 1c also indicated that densely packed grains were formed on the soda-lime glass (SLG)/Mo substrate. Large grains with a size comparable to the film thickness ($\approx 1 \pm 0.2 \mu m$) are clearly seen from the figure. The dramatic change observed in the morphology of the grown SnS films is illustrated schematically in Figure 1d.
Phase identification of the cube-like SnS thin films was conducted using XRD. Figure 1e shows the normal θ–2θ XRD pattern of the SnS grown on the SLG/Mo substrate. The lines in the bottom panel are the reported powder diffraction patterns for orthorhombic SnS (JCPDS No. 39-0354), orthorhombic Sn$_2$S$_3$ (JCPDS No. 14-0619), and hexagonal SnS$_2$ (JCPDS No. 23-0677), respectively. The diffraction peaks matched well with those reported for the orthorhombic SnS. No peaks were observed from 10°–20°, where strong peaks for Sn$_2$S$_3$ and SnS$_2$ would be located. In addition, a peak corresponding to the (040) plane of SnS was notably not observed.

Importantly, a more random orientation was observed for the cube-like SnS of Figure 1e compared to the plate-like SnS films grown at 600 and 700°C under 2 mTorr conditions (Figure S4, Supporting Information), which were also identified as pure SnS. The preferred (101) orientation became more dominant with decreasing growth pressure and also with increasing growth temperature, based on the calculated Lotgering factors (Figure S5a, Supporting Information). This observation is closely related to the evolution of the SnS plates perpendicular to the substrates (Figure S5b, Supporting Information). We also performed glancing-angle XRD, and only peaks from orthorhombic SnS were recorded (Figure S6, Supporting Information).

Raman spectroscopy was also used to detect any existing secondary phases that would not be detected by XRD. In Figure 1f, the characteristic peaks for SnS can be seen at 51, 94, 214, and 223 cm$^{-1}$.[26,41] Again, peaks at 302 and 313 cm$^{-1}$, which are indicative of Sn$_2$S$_3$ and SnS$_2$ phases, were not recorded. Based on the XRD and Raman analyses, we concluded that a phase-pure SnS thin film with a favorable flat and dense morphology was successfully formed by VTD.

When SnS evaporates congruently from the source powder at an elevated temperature of 600°C,[38] it should travel along the growth chamber toward the pumping line. We noticed that no growth of SnS ever occurred on the furnace wall within the heating zone where the target temperature is maintained. It was inferred that the evaporated SnS molecules traveled down the chamber, repeatedly condensing and re-evaporating, and finally condensed and nucleated in the region with lower temperature, where the substrates were intentionally located in the present study (see Figure S7 of the Supporting Information for the recorded temperature profiles during growth).

Crystal growth proceeds by minimizing the surface energy. Unless the evaporated SnS molecules were kinetically limited (i.e., if the diffusion length was long enough and therefore close to thermodynamically stable conditions), plate-like SnS would form predominantly, resulting in more (040) surfaces bonded by van der Waals forces, since this surface is known to have the lowest surface energy.[24,38] As the growth temperature was increased (or the growth pressure was decreased), the nucleation was more facilitated and the grain growth tended to

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**Figure 1.** Plan-view SEM images of SnS films grown at a) 2 mTorr and b) 1.4 Torr, respectively. c) Cross-sectional SEM image of SnS grown at 1.4 Torr. d) Schematic image of the change in morphology of SnS from plate-like (low pressure) to cube-like (high pressure). e) XRD pattern of the SnS thin film grown at 1.4 Torr. The lines in the bottom panel show the powder diffraction patterns of SnS, Sn$_2$S$_3$, and SnS$_2$. The slight hump at ≈36° is due to the k$_{beta}$ peak of the Mo substrate. e) Raman spectrum for the SnS thin film grown at 1.4 Torr.
occur with a plate-shape that exhibited planes with the surface normal (040), which are perpendicular to the substrate-normal direction (see Figure S5b, Supporting Information). The SnS formed at 700 °C under 2 mTorr was more similar to this case. This is in line with the prominent evolution of parallel SnS plates with a preferred (101) orientation (Figures S1a–c and S5, Supporting Information).

By contrast, as the diffusion length was decreased due to the increased deposition flux with the increased growth pressure, the evaporated SnS molecules unavoidably tended to meet quicker forming immobile seeds for nucleation. It finally leads to the formation of more cube-like shape along with a relatively random orientation (Figure 1b; Figure S5a, Supporting Information). This was also accompanied by decreased film thickness (~1 µm for 1.4 Torr and 4 µm for 2 mTorr at 600 °C).

To investigate the effect of the SnS morphology on the performance of the TFSCs, SnS/CdS heterojunctions were fabricated using CBD-CdS. Four samples were prepared at 600 °C with different growth pressures: 2 mTorr, 200 mTorr, 800 mTorr, and 1.4 Torr (see Figure S8 of the Supporting Information for plan-view SEM images of the SnS films grown at 200 and 800 mTorr). Representative photographs and a cross-sectional SEM image of the SnS TFSCs fabricated at 1.4 Torr are shown in Figures S9 and S10 of the Supporting Information.

Figure 2a shows the corresponding current density–voltage (J–V) characteristics of the four fabricated SnS TFSCs under 1 sun illumination. As the growth pressure was increased from 2 mTorr to 1.4 Torr, a dramatic improvement in cell performance was observed; the $V_{oc}$, $J_{sc}$, FF, and efficiency ($\eta$) increased from 0.022 V, 10.6 mA cm$^{-2}$, 0.258, and 0.06% to 0.320 V, 17.7 mA cm$^{-2}$, 0.564, and 3.19%, respectively. The detailed device parameters are summarized in Table 1. More J–V curves for the optimized condition of 1.4 Torr are shown in Figure S11 of the Supporting Information. The improvement in efficiency was revealed to be mainly due to the increased $V_{oc}$ value along with the increased FF and illuminated shunt resistance ($R_{sh}$). In particular, the illuminated $R_{sh}$ increased by more than a factor of 42.3 when the growth pressure was increased from 2 mTorr to 1.4 Torr.

The $J$–$V$ characteristics under the dark condition, shown in Figure 2b, also suggested an improvement in the shunt component under reverse bias. The semilog plot of $J$–$V$ for two representative devices (2 mTorr and 1.4 Torr) inset in the figure shows the difference more clearly. The reverse dark saturation current density ($J_0$) and the diode ideality factor ($n$) improved from $1.37 \times 10^{-2}$ to $8.23 \times 10^{-2}$ A cm$^{-2}$ and from 2.25 to 1.32, respectively (see Figure S12 and Table S1 of the Supporting Information for all four devices).

We attributed the improvements in $R_{sh}$ and the diode quality to the cube-like morphology of SnS. SnS absorbers with a sharp and plate-like morphology could be prone to increased recombination (i.e., increased $J_0$), probably due to the increased effective junction area. The favorable morphology of the SnS grown at 1.4 Torr, with a flat and dense surface, can therefore improve $R_{sh}$, $J_0$, and $n$.

The obtained $V_{oc}$ of 0.320 V is the second highest value among SnS/CdS TFSCs to our knowledge; Avellaneda et al. reported a $V_{oc}$ of 0.370 V using a CBD-SnS/CdS heterojunction. They considered their cell, however, exhibited a poor $\eta$ of 0.2% due to limited current collection ($J_{sc} = 1.23$ mA cm$^{-2}$). The high $V_{oc}$ of over 0.3 V for the SnS/CdS junction signifies the high quality of the SnS film grown by VTD with a controlled morphology.

Our result also suggested that a favorable morphology with limited shunt paths is a prerequisite to obtain efficient SnS TFSCs. A similar result was also reported by Steinmann et al. They reported the empirical relationship between the illuminated $R_{sh}$ and $V_{oc}$ values; the measured $V_{oc}$ (<=0.3 V) appeared

![Figure 2](image_url)

**Figure 2.** a) $J$–$V$ characteristics of the four fabricated devices with different growth pressures under 1 sun illumination; 2 mTorr, 200 mTorr, 800 mTorr, and 1.4 Torr. b) Corresponding $J$–$V$ characteristics under the dark condition. The inset is a semilog plot of $J$–$V$ curves for SnS devices grown at 2 mTorr and 1.4 Torr, exhibiting improvement in the shunt resistance in reverse bias.
to be proportional to the illuminated $R_{sh}$ ($<\approx 30$ ohm cm$^2$). Experimentally, they circumvented this issue by adding a dense overlayer of smaller SnS grains by ALD on top of the thermally evaporated larger SnS grains, which led to an increase in the $V_{oc}$ from 0.3508 to 0.3706 V, when matched with the ALD-Zn(O,S):N buffer layer.$^{[30]}$

Meanwhile, the existence of the CdS buffer layer itself was crucial for obtaining 3.19% efficiency, although it may not be an optimal partner for SnS absorbers in terms of CBO.$^{[36]}$ Without the buffer layer, the efficiency decreased sharply to 0.12% (Figure S13, Supporting Information).

Figure 3a shows a low magnification TEM image of the optimized cell structure of SLG/Mo/SnS(1.4 Torr)/CdS/i-ZnO/AZO. Each layer was clearly defined, and the energy dispersive X-ray spectroscopy (EDS) mapping and the line profile further confirmed the separation of the constituent layers (Figure S14a–c, Supporting Information). The thickness of the SnS varied locally from $\approx 940$ to 1370 nm, which was roughly consistent with the SEM image of Figure 1c. Notably, the existence of large SnS grains was confirmed from the image. Voids were intermittently observed near the interface with Mo, which could be due to the large variation in temperature during the heating and cooling of the substrate. It can be seen from Figure 3b that an abrupt junction was formed between the CdS and the SnS layers (see Figure S14c, Supporting Information). The thickness of the CdS layer was estimated to be $\approx 70$ nm. Interestingly, an MoS$_2$ layer with $\approx 6$ nm thickness was observed between the SnS and the Mo layers, as shown in Figure 3c. The lattice distance of $\approx 0.61$ nm corresponded to the (002) plane of MoS$_2$. An MoS$_2$ layer is frequently observed in CIGS or CZTS TFSCs owing to the high pressure sulfurization process; however, there are no detailed studies of the formation of MoS$_2$ in SnS TFSCs yet. Obviously, future work is needed to determine its effect on the overall device performance in SnS TFSCs.

Figure 3d–f shows the high-resolution TEM images of the SnS grains. Here, Figure 3e,f corresponded to the magnified images of regions X and Y as indicated in Figure 3d. Perfect SnS lattices were observed near the grain boundaries, and no other secondary phases were found from the fast Fourier transform (FFT) image as well. In addition, no prominent changes in the Sn and S concentrations were observed between the two SnS grains from the EDS line profile (Figure S14d, Supporting Information). Figure 3g is the selected area diffraction pattern of region Z in Figure 3d with the [100] zone axis, which again confirmed the phase purity of the VTD-SnS.

Capacitance–voltage ($C$–$V$) measurement was carried out to understand the physical properties of the champion cell. From the intercept of the $C$–$V$ plot in Figure 4a, the built-in potential of the device ($V_{bi}$) was estimated to be $0.34 \pm 0.03$ V, which was slightly higher than the recorded $V_{oc}$ of the champion cell. Here, the relative permittivity of SnS was set to 40.$^{[37,43]}$ The depletion width of the device at zero bias was estimated to be $\approx 80$ nm (Figure S15, Supporting Information). The relatively small depletion width was ascribed to the high carrier concentration of the SnS absorber; the apparent carrier concentration was calculated to be $2.4 \times 10^{17}$ cm$^{-3}$. The estimated carrier concentration was similar to that of the thermally evaporated SnS reported by Mangan et al.$^{[22]}$ In addition, carrier concentration and mobility were estimated by Hall measurement, which were $5.1 \times 10^{16}$ cm$^{-3}$ and 9.4 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. Slightly lower
carrier concentration compared to that from C–V measurement indicated that upper region of the SnS absorber close to the film surface could have higher defect density. Meanwhile, the carrier concentration of the SnS film of the 4.36% record cell was reported to be 5.7 × 10^{15} \text{cm}^{-2}.\text{[17]} To further increase the current collection, control of the intrinsic doping level of SnS is needed. For instance, NaSn has been reported to act as the current collection, control of the intrinsic doping level of SnS. The obtained full band alignment is illustrated in Figure S17, Supporting Information. Notably, a large bandgap of 2.63 eV was reported for SnS.\text{[39]} The bandgap of the SnS absorber was analyzed using UPS. The work function, conduction band minimum, and valence band maximum of the SnS were estimated to be 4.21, 3.34, and 4.66 eV below the vacuum level, respectively (see Figure S16, Supporting Information). The valence band maximum of 4.66 eV was similar to the value of 4.71 eV reported by Whittles et al.\text{[16]} In addition, the complete band structure between the SnS/CdS heterojunction was estimated through XPS using the Kraut method (Figure S17, Supporting Information). The bandgap at the junction interface (E_g,int.) was calculated to be 0.84 eV. Temperature-dependent J–V measurements under the illuminated condition were performed to investigate the dominant mechanism of recombination for the champion SnS/CdS device, as shown in Figure 5b. The extrapolation to temperature at 0 K indicates the activation energy (E_A) of J_0,\text{[50]} which corresponded to 0.76 eV. This value was in good agreement with the obtained E_g,int. value of 0.84 eV. Clearly, the E_A was lower than the E_g of SnS (1.32 eV), which suggested that the SnS/CdS interface could be the dominant recombination site.

To our knowledge, this is the first report on the long-term stability of VTD-SnS absorbers. The efficiencies for our SnS/CdS champion cell as well as those of other reported cells including CdS- and Zn-based buffers are summarized in Table S2 of the Supporting Information. Recently, Polizzotti et al. reported the improved carrier lifetime of thermally evaporated SnS thin films fabricated using extremely pure SnS source materials with minimal amounts of Co, Fe, and Mo (6N purity).\text{[51]} This result presents a possible
means of improvement for our current device by using a higher purity source for the VTD-SnS. The efficiency could be further increased by adopting proper interfacial modification, i.e., the formation of an SnO2 layer[17] or by surface treatment with etchants. Usage of more favorable n-type buffer layers such as Zn(O,S)[17,18,37] or (Zn,Mg)O [29,52] will obviously be beneficial for further improvement of the Voc value by minimizing inter - face recombination with increased Eg, int. Finally, more attention should be paid to finding a better back contact metal than Mo.[53]

In summary, facile control of the morphology of inherently anisotropic SnS was demonstrated via regulated growth kinetics during VTD. The growth of highly phase-pure orthorhombic SnS without any detectable SnS1 or SnS2 secondary phases was confirmed using XRD, Raman spectroscopy, and TEM. High temperature growth also led to the formation of micrometer-size SnS, as revealed by SEM and TEM, which is favorable for efficient TFSCs. The importance of the SnS morphology was experimentally verified from the overall improvement in cell performance for the SnS/CdS heterojunction. The efficiency of the champion cell was 2.984% (measured at the KIER, Voc = 0.3068 V). A high stability, with up to 98.5% of the initial efficiency being retained, was confirmed for the first time, and the certified efficiency after six months of storage in air was 2.938% (Voc = 0.2912 V, Jsc = 17.76 mA cm⁻², FF = 0.5680). Although an unfavorable CdS layer was used as an n-type buffer layer without any interfacial modification, the high Voc of close to 0.3 V suggests the excellent quality of the SnS thin films grown by VTD. Our approach to controlling the shape and morphology of SnS can potentially be applied to other emerging chalcogenide absorbers with inherent anisotropy.

**Experimental Section**

**Vapor Transport Deposition:** Tin sulfide was grown on one square inch SLC/Mo substrates in a conventional one-zone furnace (S&R Korea, SRVF-LV-3B-1508, see the Supporting Information) using the VTD method. The heating zone of the furnace was 200 mm. The as-received SnS powder amounting to 0.3 g (iTasco, LT40SNS312, 99.99%) was loaded in a ceramic boat, which was placed in the middle of the heating zone. The SLG/Mo substrates were placed near the edge of the heating zone close to a pumping line (≈100–110 mm from the center of the source, see Figure S2, Supporting Information). After loading the substrate on the substrate holder, the chamber was evacuated to a base pressure of

<table>
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<th>Date</th>
<th>Voc [V]</th>
<th>Jsc [mA cm⁻²]</th>
<th>FF</th>
<th>η [%]</th>
<th>Rsh [ohm cm²]</th>
<th>Rs [ohm cm²]</th>
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<tr>
<td>Initial</td>
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<td>17.25</td>
<td>0.5639</td>
<td>2.984</td>
<td>3.11</td>
<td>121.6</td>
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<tr>
<td>After 6 months</td>
<td>0.2912</td>
<td>17.76</td>
<td>0.5680</td>
<td>2.938</td>
<td>3.03</td>
<td>136.5</td>
</tr>
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MgF2 AR coating was used; *Measured on 12-20-2016; † Measured on 7-4-2017.
The measurement was conducted again after storage of the champion cell calibration technique has been established,[54] using a Keithley 236 SourceMeter system, respectively. The standard V–J data were collected at 100 kHz – used. The focused ion beam lift-out technique was used for the sample preparation. Room temperature C–V data were collected at 100 kHz using an impedance analyzer (Hewlett Packard, HP4284). The spectral response was used for the measurement of EQE (Jasco, CEP-25BX) of the solar cells. UPS equipped with XPS (Kratos, AXIS-Nova Ultra DLD) was used for the analysis of the work function of SnS and the band structure of SnS/CdS (see details in the Supporting Information). A UV–vis–NIR spectrophotometer (Varian, Cary 500) was used to measure the reflectivity of SnS thin film (SLG/Mo/SnS) as well as the fabricated cell (SLG/Mo/SnS/CdS i/ZnO/AZO).

J–V Measurement at the KIER: The champion cell was independently characterized at the KIER in Korea, where a primary reference solar cell calibration technique has been established,[54] using a Keithley 236 SourceMeter and a class AAA solar simulator (WACOM, WXSS-1555-L2) under AM 1.5G 1-sun standard conditions. The measurement was conducted after the deposition of an AR coating of ~100 nm thick MgF2.

The measurement was conducted again after storage of the champion cell in an air environment for about six months without any sealing.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Keywords
 absorbers, morphology, thin film solar cells, tin monosulfide (SnS), vapor transport deposition

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Kinetically Controlled Growth of Phase-Pure SnS Absorbers for Thin Film Solar Cells: Achieving Efficiency Near 3% with Long-Term Stability Using an SnS/CdS Heterojunction

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Supporting Information

**Kinetically Controlled Growth of Phase-pure SnS Absorbers for Thin Film Solar Cells: Achieving Efficiency Near 3% with Long-term Stability Using a SnS/CdS Heterojunction**

*Dongha Lim, Hoyoung Suh, Mahesh Suryawanshi, Gwang Yeom Song, Jae Yu Cho, Jin Hyeok Kim, Jae Hyuck Jang, Chan-Wook Jeon, Ara Cho, SeJin Ahn, and Jaeyeong Heo*
Use of one-zone furnace: A two-zone furnace was initially tested to independently and reliably control the source and substrate temperatures. However, we observed that the growth of SnS mainly occurred in a blind spot in-between two heating zones with a size of ~5 cm, where no heating coils are present (see figure below, a pressure of 2 mTorr was used with a long diffusion length). We speculated that a dramatic drop in temperature was critical to form SnS. In this case, we observed a narrow and gradual distribution of SnS (gray), Sn$_2$S$_3$ (gray/black), and SnS$_2$ (yellow) by XRD, which was similar to that reported by Wangperawong et al. This narrow distribution was not suitable for growing pure SnS on a large 2.5 cm × 2.5 cm substrate with good uniformity or for subsequently fabricating the solar cells. Therefore, we used a one-zone furnace instead, as discussed in the main manuscript, and tried to optimize the uniform growth of the VTD SnS for a larger size in a controlled manner. The use of a two-zone furnace without a blind spot between two heating zones will be beneficial to improve the thickness uniformity in a follow-up study.
**Band structure calculation:** The UPS spectra were recorded using He-Iα radiation (UPS, $h\nu = 21.22$ eV). The work functions (WF) were determined from the secondary electron cut-off (SEC) using the equation $WF = 21.22$ eV – SEC (see Figure S16). The differences between the Fermi levels and valence band maximum ($E_{VBM}$) were determined from the low binding energy onset.

For XPS measurements, the X-ray source was monochromated Al-Kα (1486.68 eV) with binding energy calibration. The depth profiling data were obtained by mildly sputtering the SnS/CdS surface with 1 keV Ar$^+$ ions. The band gaps of SnS and CdS were extracted from the EQE data in Figure 4b.

The valence band offset ($\Delta E_V$) of the SnS and CdS heterojunction was estimated using the Kraut method (see Figure S17) using the core level offset from the SnS/CdS heterojunction.$^{[12-4]}$

\[
\Delta E_V = E_{V}^{SnS} - E_{V}^{CdS} = (E_{Sn 4d}^{SnS} - E_{Cd 4d}^{CdS}) - (E_{Sn 4d}^{SnS} - E_{V}^{SnS}) + (E_{Cd 4d}^{CdS} - E_{V}^{CdS}),
\]

where the binding energy difference between the Sn 4d and Cd 4d core levels at the SnS/CdS interface ($E_{Sn 4d}^{SnS} - E_{Cd 4d}^{CdS}$) was calculated to be 13.78 eV (i.e., 25.43 eV–11.65 eV), the binding energy difference between Sn 4d in the bulk SnS with respect to its valence band maximum ($E_{Sn 4d}^{SnS} - E_{V}^{SnS}$) was measured to be 25.04 eV (i.e., 25.2 eV–0.16 eV), and finally, the binding energy difference between Cd 4d in the bulk CdS with respect to its valence band maximum ($E_{Cd 4d}^{CdS} - E_{V}^{CdS}$) was estimated to be 9.68 eV (i.e., 11.5 eV–1.82 eV). Thus, $\Delta E_V$ was determined to be -1.58 eV.

Finally, the conduction band offset ($\Delta E_C$) was calculated using the bandgap values of SnS (1.32 eV) and CdS (2.42 eV) estimated from EQE and the estimated value of $\Delta E_V$ according to the following formula,

\[
\Delta E_C = (E_g^{CdS} - E_g^{SnS}) + \Delta E_V
\]
where $\Delta E_c$ was determined to be $-0.48$ eV.
Figure S1. a) Low-magnification and b) high-magnification plan-view SEM images for the SnS grown at 700 °C with a growth pressure of 2 mTorr. c) The corresponding cross-sectional SEM image of the SnS grown at 700 °C. d) Plan-view SEM image for SnS grown at 500 °C with a growth pressure of 2 mTorr.
Figure S2. a) Photograph of the one-zone furnace after the growth of SnS at 600 °C with a growth pressure of 1.4 Torr. Notably, no growth occurred within the heating zone. b) An enlarged photograph of the SLG/Mo substrate with a substrate holder after the SnS growth. SnS was uniformly formed with a 2.5–3 cm length as inferred from the color of the film. The plan-view SEM image of location (1) is shown in Figure 1b. Morphology of the SnS film at location (2) is shown in c). The uniformity of the thickness between locations (1) and (2) at 1.4 Torr condition was estimated to be ~70–75% from SEM. Obviously, the uniformity can be further improved by optimizing the furnace design, i.e., the gas flow and temperature profiles.
the use of a vertical-type commercial VTD chamber, or the use of a blind-spot-free two-zone furnace (as discussed above). While a more favorable morphology was obtained at increased growth pressure, the opposite tendency was observed for the uniformity of the thickness. As the growth pressure was decreased to 2 mTorr, better thickness uniformity along the substrate was obtained. When the process pressure was increased above 1.4 Torr, however, a large decrease in the growth rate along with worse thickness uniformity was obtained. Therefore, 1.4 Torr was fixed to be the upper limit for the growth pressure in the present study for the device fabrication of solar cells.
Figure S3. Low magnification plan-view SEM image of the SnS film grown at 1.4 Torr, demonstrating the uniformity of the SnS over a large area.
Figure S4. Normal $\theta$–$2\theta$ XRD patterns of the SnS films grown at 500, 600, and 700 °C, along with the known diffraction pattern of powder SnS (growth pressure of 2 mTorr). Little or no growth occurred at 500 °C, and an amorphous-like pattern was observed (see Figure S1d). As the growth temperature was increased from 600 to 700 °C, the (101)-preferred orientation predominated, which was consistent with the corresponding plan-view images in Figure 1a (600 °C) and Figure S1a-b (700 °C).
Figure S5. (a) Change in the Lotgering factors ($F$) of the main peaks located at 20–35° for the SnS films grown at 600 °C and at 1.4 Torr and 2 mTorr, and the SnS film grown at 700 °C and 2 mTorr. $F$ was calculated based on the XRD data shown in Figure 1e and Figure S4. A gradual increase is noted particularly for $F_{(101)}$, indicating the change in morphology. (b) Schematic drawing of plate-shape SnS grown in the (101) preferred orientation. The normal direction of the (040) plane is perpendicular to the normal of the SLG/Mo substrate.
Figure S6. GAXRD patterns of the SnS thin film grown at a pressure of 1.4 Torr (ω = 0.3–2.0 °). Only peaks corresponding to the reported peaks for orthorhombic SnS (JCPDS No. 39-0354) are observed.
Figure S7. Temperature profiles for the furnace and locations (1) and (2) (see Figure S2b), which were measured using thermocouples in direct contact with the substrate holder.
**Figure S8.** Plan-view SEM images of the SnS films grown at a) 200 and b) 800 mTorr. More densely formed SnS is observed to have grown at a pressure of 800 mTorr.
**Figure S9.** Photographs of a) the SLG/Mo/SnS sample grown at 600 °C under 1.4 Torr and b) the fabricated cells with a SLG/Mo/SnS/CdS/i-ZnO/AZO/Ni/Ag structure.
Figure S10. Cross-sectional SEM image of the fabricated cells with SnS grown at 1.4 Torr (SLG/Mo/SnS/CdS/i-ZnO/AZO). Large grains of SnS are observed in this image.
Figure S11. $J$–$V$ curves for twelve representative cells with the optimized conditions of 1.4 Torr at 600 °C under 1-sun illumination condition. Variation among the cells mainly resulted from $V_{oc}$, which may be ascribed to the slight change in the SnS morphology due to variation in the substrate temperature depending on the location (see Figure S2 and S7).
Figure S12. $J$–$V$ characteristics of the four devices under the dark condition with different SnS growth pressures: a) 2 mTorr, b) 200 mTorr, c) 800 mTorr, and d) 1.4 Torr. The shunt component was removed to more reliably estimate the diode parameters following the procedure proposed by Dongaonkar et al. The estimated reverse dark saturation current densities and ideality factors are summarized in Table S1.
Table S1. Simulated diode parameters of the $J-V$ characteristics of the SnS/CdS TFCSs fabricated at various deposition pressures under dark conditions; 2 mTorr, 200 mTorr, 800 mTorr, and 1.4 Torr.

<table>
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<th>device</th>
<th>$J_0$ [A cm$^{-2}$]</th>
<th>$n$</th>
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<tr>
<td>2 mTorr</td>
<td>$1.37 \times 10^{-2}$</td>
<td>2.25</td>
</tr>
<tr>
<td>200 mTorr</td>
<td>$7.74 \times 10^{-5}$</td>
<td>2.24</td>
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<tr>
<td>800 mTorr</td>
<td>$5.96 \times 10^{-5}$</td>
<td>2.19</td>
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<tr>
<td>1.4 Torr</td>
<td>$8.23 \times 10^{-7}$</td>
<td>1.33</td>
</tr>
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</table>
Figure S13. a) $J$–$V$ characteristics of four SnS solar cells without the CdS buffer layer, which were measured in-house (structure: SLG/Mo/SnS/i-ZnO/AZO/Al). Average $V_{oc}$, $J_{sc}$, FF, and $\eta$ are 0.041 V, 10.3 mA cm$^{-2}$, 0.293, and 0.12%, respectively. Here, the same X and Y scales are used for direct comparison with Figure 2a. b) EQE of the devices, with a maximum of $\sim$45%. 
Figure S14. a) STEM image of the Mo/SnS/CdS/i-ZnO/AZO structure and the corresponding EDS mapping images of Zn, O, Cd, Sn, S, and Mo. It can be seen from the mapping images that the elements of each thin film are clearly separated. b) TEM image showing the acquired EDS line profiles of Line 1 between two SnS grains and Line 2 between SnS/CdS/i-ZnO/AZO stacks. c) and d) correspond to the elemental profiles of Lines 1 and 2, respectively. A slight increase in the oxygen peak was noted at the SnS/CdS interface, which could be due to ambient oxidation of the SnS surface and/or oxidation from oxygen impurities during the CBD-CdS process.
Figure S15. Carrier concentration profile obtained from the $C$–$V$ measurement for the champion cell.
Figure S16. a) UPS spectrum of SnS. The inset shows the magnified view of the secondary electron cut-off energy of 17.01 eV, which was determined from the intersection of the linear portion of the UPS spectrum and the baseline. The work function of SnS was calculated to be 4.21 eV. b) Magnified view of the low binding energy region in the UPS spectrum for $E_{\text{VBM}}$ determination (0.45 eV). The $E_{\text{VBM}}$ was estimated to be -4.66 eV with respect to the vacuum level ($E_{\text{VAC}}$). The conduction band minimum ($E_{\text{CBM}}$) was further calculated to be -3.34 eV by adding the SnS band gap energy of 1.32 eV to the $E_{\text{VBM}}$. 
Figure S17. a) XPS spectrum of CdS deposited on the SnS absorber layer, which was etched using Ar$^+$ ions to reveal both Sn 4d and Cd 4d peaks. b) VB XPS spectrum of SnS. c) Magnified view of the low binding energy region in the VB XPS spectrum of SnS for $E_V$ determination (0.16 eV). d) VB XPS spectrum of CdS deposited on the FTO substrate. e) Magnified view of the low binding energy region in the VB XPS spectrum of CdS deposited on FTO for $E_V$ determination (1.82 eV).
Figure S18. Measured reflectivity of the SnS grown on a SLG/Mo substrate and the final device with SLG/Mo/SnS/CdS/i-ZnO/AZO. Reflectivities of less than 1.5% were recorded throughout the entire wavelength range from 200 – 1200 nm.
Figure S19. Certification of the champion cell ($\eta = 2.938\%$) measured at the KIER in Korea.
Table S2. Efficiency table summarizing the reported orthorhombic SnS-based TFSCs with $\eta > 1\%$.

<table>
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<th>author</th>
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<th>growth method for SnS</th>
<th>$E_g$ of SnS [eV]</th>
<th>$p$-$n$ junction</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF</th>
<th>$\eta$ [%]</th>
<th>$R_s$ [ohm cm$^2$]</th>
<th>$R_{sh}$ [ohm cm$^2$]</th>
<th>area [cm$^2$]</th>
<th>measurement</th>
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<td>CdS buffers</td>
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<td>SnS/CdS</td>
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<td>0.435</td>
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<td>213</td>
<td>0.23</td>
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<td>0.564</td>
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<td>3.21</td>
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<td>2.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>SnS/Zn(O,S):N$^{c)}$</td>
<td>0.26</td>
<td>18.7</td>
<td>0.51</td>
<td>2.50</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>SnS/SnO$_2$/Zn(O,S):N$^{d)}$</td>
<td>0.372</td>
<td>20.2</td>
<td>0.58</td>
<td>4.36$^e)$</td>
<td>-</td>
<td>-</td>
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<td>0.3341</td>
<td>20.645</td>
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<td>0.66</td>
<td>74</td>
<td>0.25</td>
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<td>2.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>in-house</td>
<td>[13]</td>
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</table>

$^{a)}$ MgF$_2$ AR coating was used; $^{b)}$ the measurement was carried out after the storage of the sample in air for about six months; $^{c)}$ interfacial SnO$_2$ was not formed; $^{d)}$ ~0.5 nm-thick interfacial SnO$_2$ was formed by H$_2$O$_2$ treatment; $^{e)}$ current world-record efficiency for SnS-TFSCs.
References for SI