Sb₂Se₃ Solar Cells



Tunable Quasi-One-Dimensional Ribbon Enhanced Light Absorption in Sb₂Se₃ Thin-film Solar Cells Grown by Close-Space Sublimation

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The non-cubic antimony chalcogenides, i.e., Sb_2Se_3 , formed by quasi-onedimensional ribbons can enhance light absorption and carrier transport by tuning the ribbon direction using the close-space sublimation (CSS) deposition. The improved device performance is found to be associated with the ribbon direction, which was investigated with theoretical calculation and experimental optical measurement in the Sb_2Se_3 films and devices. Decent device efficiency could be achieved when the ribbons were tuned to be as normal to the substrate as possible. The substrate temperature and film thickness are critical for the fine-tuning of ribbon orientations during the CSS deposition. Our results show that [211]-preferred orientation leads to the minimum series resistance and highest light absorbance in the device. This observation demonstrates that Sb_2Se_3 -like quasi-one-dimensional materials with van der Waals boundaries can achieve scalable production at low cost and hold great potential for next-generation solar cell using the recently developed vapor transport deposition technology.

1. Introduction

Thin-film solar cells provide affordable, renewable and sustainable energy.^[1,2] However, it is necessary to develop next-generation photovoltaic technology using environmentally-benign and earth-

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abundant materials with high power conversion efficiency (PCE).^[3,4] Thin-film chalcogenide photovoltaics (PV) technologies have been dominating the thin-film PV market, among which *First Solar*'s CdTe technology and *Solar Frontier*'s copper–indium– gallium–selenium (CuInGaSe, CIGS) solar cells provide the most successful commercial products with certificated cell efficiency of over 22%.^[4] However, the toxicity of Cd, the limited earth storage of Te, and the high cost of In and Ga pose significant barriers to achieving the needed PV module capacity beyond terawatt.

New PV technology is highly demanded. For example, copper–zinc–tin–sulfur $(CZTS)^{[5,6]}$ and perovskite solar cells (e.g., $CH_3NH_3PbI_3)^{[7,8]}$ have shown promising PCE. Nevertheless, these candidates suffer from several issues such as stability, defect control, environmental concern (e.g. Pb in perovskite solar cells), and high

manufacturing cost.^[2,3] To address these challenges, non-cubic chalcogenides with non-toxic and earth-abundant elements, such as Sb₂Se₃ and Sb₂S₃, have shed light on new thin-film PV systems.^[9–12] These layered materials exhibit unique crystal structure, i.e., consisting of quasi-one-dimensional ribbons weakly bonded by van der Waals forces, e.g., $(Sb_4Se_6)_n$ ribbons in Sb₂Se₃.^[13] The ribbon-like structure leads to highly anisotropic charge transport (i.e., directional transport behavior) compared with the traditional cubic solar cell materials with isotropic transport (e.g., CdTe, CIGS, and perovskites).^[14] Meanwhile, it is believed that the anisotropic growth can also benefit the light absorption.

The anisotropic nature of these ribbon-like chalcogenides, though potentially beneficial to solar cell performance, requires careful synthesis to suspend the needle or flake growth.^[13] To overcome this challenge, various growth technologies were introduced for antimony chalcogenides. For example, Tang's team has demonstrated that Sb₂Se₃ solar cells can achieve a PCE of 6% with rapid thermal evaporation (RTE), where Sb₂Se₃ melts and evaporates from the liquid phase;^[11,12] Seok's team successfully fabricated Sb₂S₃ sensitized solar cells with 6.4% PCE using solution-based technology.^[15,16] However, these approaches are not fully compatible with high-throughput manufacturing technology. For example, commercial CdTe



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technology from *First Solar* is based on a vapor transport deposition (VTD) process,^[17] which is on a par with the close-space sublimation (CSS) process for CdTe manufacturing and allows for high-throughput deposition onto moving sub-strates.^[18,19] Meanwhile, CSS technique directly vaporizes the solid raw materials, which has been widely used in the lab to achieve the scalability of chalcogenide photovoltaics and could greatly reduce the cost.

In this work, we theoretically investigate the anisotropic electronic and optical properties of Sb_2Se_3 , and experimentally demonstrate that the quasi-one-dimensional ribbons can be tailored by varying CSS growth conditions. We show that [211]-oriented Sb_2Se_3 exhibits the best device performance with 4.27% PCE, which is in agreement with the theoretical understanding. In addition, the success of CSS technology in the non-cubic anisotropic materials opens up avenues for integrating these ribbon/layer-like materials into the most successful large-scale chalcogenide solar cell manufacturing process. Our work further confirms the great potential of Sb_2Se_3 as a low-cost, environment-friendly, scalable emerging thin-film PV for affordable solar energy.

2. Results and Discussion

To obtain ideal Sb_2Se_3 crystal structure, we first conduct structure optimization using first-principles density-functional theory (DFT). As there are significant van der Waals (vdW) interactions between $(Sb_4Se_6)_n$ ribbons, the lattice constants and atomic coordinates were optimized using vdW functional, which

shows good agreement with the experiments. As shown in **Figure 1**a,b, the one-dimensional $(Sb_4Se_6)_n$ ribbons stack along c axis (here, [001] direction) by strong Sb-Se bonds, while the ribbons are weakly bonded by vdW forces along a and bdirections, without dangling bonds, in agreement with the results of Zhou et al.^[12] Figure 1c-e illustrate the carrier transport along $(Sb_4Se_6)_n$ chains in different orientations. When the $(Sb_4Se_6)_n$ ribbons are grown with (120) plane parallel to the substrate (as illustrated in Figure 1c), the vdW gap between the ribbons will exert potential barriers for carrier transport towards top and bottom substrates where carriers are collected. However, when the ribbons are [211] and [221]-oriented on top of the substrate (Figure 1d,e), the charge carrier can easily transport along the ribbons, which will reduce photogenerated carrier recombination (note that we use the "[hkl]-oriented direction" to denote the (hkl) plane normal direction). Obviously, the series resistivity is much higher in [120]-oriented grain than in [211]and [221]-oriented grains.^[12] Therefore, to promote the carrier transport and improve the device performance, these $(Sb_4Se_6)_n$ ribbons should be grown normal to the substrate, e.g., [211] and/ or [221] direction, as shown in Figure 1f,g. Additionally, the [211] oriented grain in principle should be better than [221] oriented grain in terms of charge transport, because the angle between the ribbon and the surface is 52.6° in the [211] oriented grain, higher than 46.1° in the [221] oriented grain (Figure 1f,g).

To achieve the desired ribbon direction, it is critical to control the growth condition. Prior to performing the CSS growth of Sb_2Se_3 (as shown in Figure 2a), we first check its phase diagram, thermal behavior, and sublimation behavior, then calculate the



Figure 1. Sb_2Se_3 van der Waals crystals with tunable ribbons (Sb_4Se_6)_n showing anisotropic transport behavior. a, b) Atomic configuration from the side and top view, respectively. c-e) Atomic structures of [120], [211], and [221]-oriented Sb_2Se_3 grains on the CdS-coated FTO glass substrate. f, g) Comparison between [211] and [221]-oriented grains on CdS substrate. The ribbons in the [211]-oriented grains are aligned closer to the plane normal compared to the ribbons in the [221] oriented ones, suggesting a more facile carrier transport along [211]-oriented grains.



vapor pressure of the Sb₂Se₃ (liquid), Sb₂Se₃ (solid) and Se vapor. The sublimation process is controlled by the substrate, source temperature and distance, the chamber pressure and ambient, and mean free path of Sb and Se₂ molecules. More details can be found in Supporting Information. Due to the low melting point (608 °C) of Sb₂Se₃ and the high saturated vapor pressure (≈100 Pa at 550 °C),^[20,21] (see details in Supporting Information) it is suitable to conduct CSS deposition. Compared to the successful RTE deposition^[12] evaporated from the liquid phase of Sb₂Se₃, the thin film is directly sublimated from the solids in the CSS approach.^[22] Considering the most successful CdTe technology by CSS, CdTe has a much higher melting point (\approx 1092 °C) and much lower saturated vapor pressure (\approx 0.5 Pa at 550 °C).^[23] The high vapor pressure of Sb₂Se₃ at a low temperature requires remarkably much less energy consumption during manufacturing and compatible integration to the recent CdTe thin film technologies, e.g., VTD used for synthesizing CdTe by First Solar.^[24] The Sb₂Se₃ thin film via CSS deposition grows extremely fast, $\approx 1 \,\mu m \,min^{-1}$, much faster than that of other physical vapor deposition technology (e.g., sputtering at $0.01 \,\mu m \,min^{-1}$ and thermal evaporation at $0.1 \,\mu\mathrm{m\,min}^{-1}$). The as-grown Sb₂Se₃ films were shown in Figure 2b. A window layer CdS was deposited on the F-doped SnO₂ (FTO) glass via chemical bath deposition (CBD) with various thickness (60-100 nm). The Sb₂Se₃ films show desired large-scale uniformity without pinholes, as evidenced by the view from the glass side. The crystalline structure of the CSS grown Sb₂Se₃ was investigated as a function of different growth condition and film thickness as shown in Figure 2c,d, respectively. The substrate temperature during the growth significantly impacts the orientation of Sb₂Se₃ due to its orthorhombic structure with Pbnm space group. In Figure 2c, the film thickness was fixed at 600 nm while we controlled the substrate temperature using the upper heater of CSS. The diffraction intensity with respect to the (120) peak (2θ -16.9°) and (211) peak (2 θ -28.2°) and (221) peak (2 θ -31.1°) change significantly. At low substrate temperature, such as lower than 300 °C, the (120) peak intensity is suspended. In contrast, when the substrate temperature is greater than 300 °C, the (120) peak becomes much stronger, indicating that the $(Sb_4Se_6)_n$ ribbons orientation can be tailored by the substrate temperature during the CSS deposition. Therefore, CSS has a great advantage over other approaches when tuning the ribbon orientations, which has a prominent effect on the device efficiency. Furthermore, CSS deposition of Sb_2Se_3 does not require high substrate temperature, suggesting the much less energy consumption of utilizing the soda-lime glass substrate at ~ 600 °C close to the glass transition temperature of the soda-lime glass substrate.

We grow several Sb₂Se₃ films with different thickness at identical growth condition while only changing deposition time, i.e., 30-120 s, resulting in thickness varying from 0.6 µm to 2 µm at 300 °C substrate temperature and 550 °C source temperature, as presented in Figure 2d. It shows that the (120) peak does not vary with film thickness, but the films show preferred (211) surface with increasing thickness. Here, our results demonstrate that [211]oriented grains dominate the thicker films ($>0.6 \mu m$) grown by CSS deposition, indicating that better carrier transport behavior with lower surface energy, such as the (100), (010) planes.^[12] These two planes are free of dangling bonds, indicating less recombination loss at grain boundary.^[13] The texture coefficient (TC) of the (120), (221), and (211) peaks were calculated as a function of thickness in order to quantify the orientation effect in these films (as shown in Figure 2e, see details in Supporting Information), further suggesting that the [hk0] oriented grains parallel to the substrate (TC_[hk0] < 1), while [hkl]-oriented grains ($l \neq 0$) prefer normal to the substrate ($TC_{[hkl]} > 1$). Figure 2f shows the Raman spectra for one representative Sb₂Se₃ thin film with thickness ${\approx}1.6\,\mu m$ collected at room temperature with a red laser with 632 nm wavelength. The structural and vibrational properties of Sb_2Se_3 can be observed at 187, 250, 360, 370, and 448 cm^{-1} respectively, suggesting an excellent crystalline behavior without secondary phases. The two major peaks at \approx 187 and 250 cm⁻¹ are associated with the Se-Sb-Se bending, and Sb-Se stretching,^[25] respectively, as displayed in the inset of Figure 2f.



Figure 2. a) Schematic of the Sb₂Se₃ CSS deposition. b) Photographs of CSS grown Sb₂Se₃ thin films on CdS coated FTO glass substrate. The substrate size is $2.5 \times 5 \text{ cm}^2$. c) XRD patterns for the Sb₂Se₃ deposited at different substrate temperature with fixed thickness at 600 nm. d) XRD patterns for the Sb₂Se₃ with various thickness deposited at the fixed substrate temperature of 300 °C and the fixed source temperature of 530 °C. The standard Sb₂Se₃ structure file using JCPDS 15-0861 is plotted in (c) and (d) as a reference. e) Representative texture coefficients of the diffraction peaks in Sb₂Se₃ as a function of thickness. f) Raman analysis for a Sb₂Se₃ film.



According to the cross-sectional SEM image in Figure 3a, the Sb₂Se₃ thin film with [211]-oriented grain grown by the CSS technology is dense without appreciable voids. Here, the CdS layer is grown by chemical bath deposition (≈100 nm) and Sb₂Se₃ with \approx 600 nm thickness is subsequently deposited. The elemental mapping of Cd, Se, and Sb at the cross-section of Sb₂Se₃ film is shown in Figure 3b. It suggests that the device consists of three distinct layers (i.e., FTO/CdS/Sb₂Se₃) with homogenous distribution of the elements in each layer. In particular, the Cd diffusion into the Sb₂Se₃ films is observed, in agreement with CdS/Sb₂Se₃ heterojunction deposited by RTE.^[26] The EDS spectra detected on the film surface show that atomic ratio between Se and Sb is close to 1.5 (59.8:39.2 as shown in Figure 3c). Figure 3d,e show the topography and current image of the Sb₂Se₃ thin film recorded by atomic force microscopy (AFM) and conductive AFM (c-AFM), respectively. The root-mean-square (RMS) roughness of the film is about 17 nm and the average grain size is about 500 nm. The topography has negligible impact on the current image, suggesting no artifacts in the current images originating from the topographic features. The current image collected under sample bias at +4 V shows that the conduction in Sb₂Se₃ thin film is not uniform. Remarkably, there is a clear difference between the current inside grains and at grain boundaries (i.e., the valleys of the height curve). A line scan of the topography and current image crossing the grains (Figure 3f) reveals that grain boundary shows higher resistivity while intragrains are more conductive. Such striking feature is attributed to a lower density of charge carriers at these boundaries, suggesting a selfpassivation behavior around grain boundaries with lower

formation energy.^[27] It significantly reduces the carrier recombination at grain boundaries, and benefits the carrier collection and carrier transport in grains. In addition, this validates that the parallel-stacked quasi-one-dimensional ribbons normal to the substrate that are weakly bounded by interchain vdW interactions without dangling bonds (as shown in Figure 1a) could reduce carrier recombination at grain boundaries, in contrast to cubic chalcogenide photovoltaics where $CdCl_2$ is introduced to passivate CdTe grain boundaries to reduce carrier recombination.^[28]

It is reported that Sb₂Se₃ has intrinsic indirect bandgap of \sim 1.17 eV, and direct bandgap of 1.2 eV.^[29] Here we also theoretically investigate their electronic structure. The band gap is underestimated by DFT with exchange-correlation functional under the generalized gradient approximation (GGA), e.g., 0.8036 eV for the direct gap, 0.8030 eV for the indirect gap. We therefore employed more accurate exchangecorrelation functionals, including the modified Becke-Johnson exchange potential (MBJ) and hybrid HSE06 functional. Calculation details are given in Section 4. The DFT-HSE06 yields a direct gap of 1.3469 eV and an indirect gap of 1.3366 eV, while the DFT-MBJ gives a direct band gap of 1.2388 eV and an indirect gap of 1.2236 eV. It suggests that the DFT-MBJ is sufficient to give a relatively accurate description of electronic structure (e.g., band gap) for Sb₂Se₃ with much lower computational cost. We, therefore, conduct further electronic structure investigation using the MBJ functional. The calculated band structure and orbital-resolved projected density of state (PDOS) are shown in Figure 4a. From the band structure plot, both valence band maximum and conduction band minimum



Figure 3. a) Cross-sectional scanning emission microscopy (SEM) and b) energy dispersive spectroscopy (EDS) elemental mapping of the Sb₂Se₃ device with [211]-oriented grains. c) EDS spectra of the Sb₂Se₃ film at a substrate temperature of 300 °C, showing the detected elements Cd, Se, and Sb. d) Atomic force microscopy (AFM). e) Conductive atomic force microscopy (cAFM). f) Current difference and topography along the dashed line shown in (d) and (e). The AFM and cAFM scanning area is $2.0 \times 2.0 \,\mu\text{m}^2$. The correlation between topography and conductivity of grains and grain boundaries is shown in (f).



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Figure 4. Theoretical and experimental electronic structures and optical properties of the CSS grown Sb_2Se_3 . a) Electronic structure and orbital-resolved projected density of state (DOS) determined by the DFT calculations. b) Valence charge density, indicating weak interchain van der Waals interactions. c) The calculated optical absorption when incoming light is along [120], [221], and [211] direction. d, e) The transmittance and absorbance spectra of the Sb_2Se_3 thin film where the direct and indirect bandgap were extracted. f) The experimental absorption coefficients calculated from the UV–Vis absorbance spectra for the films with [120], [221], and [211]-oriented grains.

are located on the X– Γ path. The PDOS plot further suggests that the VBM is dominated by Se-p orbitals, and the CBM consists of Se-p and Sb-p orbitals. The valence charge density shown in Figure 4b reveals that electrons are mainly located along the ribbons with minimal charge density across ribbons, indicating the presence of higher potential barrier for carrier hopping between neighboring ribbons. To further understand the impact of quasi-one-dimensional (Sb₄Se₆)_n ribbons on the optical properties, we calculate optical absorption using the independent particle approximation and the results are shown in Figure 4c. It clearly demonstrates that optical absorption depends on specific ribbon orientation. As the calculation is based on single crystal, it may not reveal the light absorption in the experimental polycrystalline films with mixed orientations. Our theoretical findings on the fundamental electronic structure were further verified by the UV-Vis spectra of CSS-deposited Sb₂Se₃ from optical characterization. Figure 4d and 4e show the measured transmittance and absorbance spectra of the Sb₂Se₃ film with CdS window layer, suggesting a strong absorption in the Sb₂Se₃ which agrees with the theoretical results. The indirect bandgap and direct bandgap extracted from the absorbance spectrum are about 1.15 and 1.2 eV for Sb₂Se₃ (2.4 eV for the CdS film also shown in the inset of Figure 4e), respectively, in good agreement with the above DFT-MBJ results. The calculated absorption coefficient as a function of the grain orientation from the absorbance measurement is shown in Figure 4f, which matches well with the theoretical predictions in terms of overall absorption (Figure 4c).

Next, we proceed to determine the dependence of the Sb_2Se_3 solar cell device performance on the orientation of $(Sb_4Se_6)_n$ ribbons. The Sb_2Se_3/CdS heterojunction solar cells were fabricated with graphite and Ag electrode (Figure 5a). The energy level alignment in the device is shown in Figure 5b, which is efficient for charge transfer (graphite work function of 5.0 eV vs. Au of 5.1 eV). The device performance with different ribbon orientation is shown in Figure 5c, and the device characteristics are listed in Table 1. Here, we select the Sb₂Se₃ films grown at different substrate temperature with various $(Sb_4Se_6)_n$ ribbon orientation (as shown in Figure 2c) for device fabrication. We focus on the orientation dependent device performance, and other contributions to the device performance, such as the improved crystallinity and reduced defects at various substrate temperature, may not be discussed here. The strong correlation between the device performance and the ribbon orientation was established through the J-V measurement. As expected, the film with [211] preferred orientation shows the best device performance with 4.27% PCE, which is originated from the improved open-circuit voltage $V_{\rm oc}$ and short-circuit current $J_{\rm sc}$. The reduced series resistance ($R_{\rm oc}$, resistance at $V_{\rm oc}$) dominates the device performance, while the shunt resistance $(R_{\rm sh})$ keeps almost constant. This device behavior can be explained by the [211] oriented grain consisting of tilted $(Sb_4Se_6)_n$ ribbons, where the carrier transport in the [211] oriented grains is more facile than in the [221]- and [120]oriented grains (as shown in Figure 1c-e and inset of Figure 5c with different vdW boundaries). This observation is in agreement with the previous RTE devices,^[12] and better device performance may be achieved using Au electrode with better ohmic contact between the metal and semiconductor than graphite paste. The higher intensity of (120) peaks indicates more $(Sb_4Se_6)_n$ ribbons parallel to the substrate, which SCIENCE NEWS __ www.advancedsciencenews.com



Figure 5. Device performance of the Sb₂Se₃ cells. a) Schematic solar cell geometry. b) Energy level diagram of the layers in the cells. c, d) The current density–voltage (*J*–*V* curve) and EQE spectra of the orientation dependent films. The inset of (c) illustrates the films with different ribbon orientation. The inset of (d) shows the histogram of device efficiencies from various fabricated devices.

significantly increases the series resistance of the device and thus lowers the device performance (e.g., reduce V_{oc} and J_{sc}). Here, we provide further evidence of the benefit from the ribbon orientation dependent light trap by the external quantum efficiency (EQE) measurement (see Figure 5d). As shown in Figure 4f, the ribbon orientation affects the optical absorption, therefore the [211] oriented grains could absorb more light in the range of 400 to 850 nm. In particular, the [211] and [221] oriented films significantly improve the light absorption than that of [120] oriented film. The photocurrent with integrated EQE is consistent with the J_{sc} determined by the J-V curve (see more details in Supporting Information).

3. Conclusion

In summary, we demonstrate that the tunable $(Sb_4Se_6)_n$ ribbon orientation can enhance the light absorption and carrier transport, and enable the Sb_2Se_3 thin film solar cells with

 Table 1. Device performance parameters of champion device with varying ribbon orientations.

Preferred grain orientation	V _{oc} , V	J _{sc} , mAcm ⁻²	FF, %	$R_{\rm oc}$, $\Omega {\rm cm}^2$	R _{sh} , Ω cm ²	PCE, %
[211]	0.421	21.74	46.65	59.25	1087	4.27
[221]	0.415	19.26	49.43	66.75	1006	3.92
[120]	0.386	18.82	39.75	144.57	1025	2.91

4.27% PCE. The Sb₂Se₃ thin film can be successfully grown by low-cost close-space sublimation. We found that the light absorption in the Sb₂Se₃ film is correlated with the ribbon direction and the device performance is significantly influenced by the orientation of the $(Sb_4Se_6)_n$ ribbons. Furthermore, the desired substrate temperature should be lower than 300 °C to prevent the [120]-oriented grain growth during CSS deposition. The latter may cause higher series resistance and lower light absorption in the device. Our results demonstrate that environment-friendly Sb₂Se₃ thin film solar cells can be manufactured in large scale at a low cost with low energy consumption thanks to the earthabundant elements and the low deposition temperature. Finally, the CSS-grown Sb₂Se₃ solar cell can be directly integrated into the recent vapor transport deposition technology for thin film photovoltaics.

4. Experimental Section

Solar Cell Fabrication: About 100 nm thick CdS window layers were deposited on a cleaned florine doped SnO_2 coated soda-lime glass (FTO, Pilkington, US) by chemical bath deposition (CBD) at a bath temperature of 70 °C. The CdS films were annealed in air at 400 °C for 30 min to improve the crystallization.

Sb₂Se₃ thin films with thicknesses of 0.6–2 µm were grown in Ar ambient using a commercial CSS system (MTI, US). The high purity Sb₂Se₃ (99.999%, Alfa Aesar, US) was placed on the bottom AlN plate, and the CdS coated FTO substrate was loaded on the top AlN plate (5 mm distance from the Sb₂Se₃ powder). To optimize the growth conditions of Sb₂Se₃ absorbers, the substrate and source temperatures were varied from 250 to 350 °C, and 500 to 580 °C, respectively at chamber pressure about 1–10 mTorr. The Sb₂Se₃ thin film thickness was controlled by varying the deposition time from 30 to 100 s, then switching off the halogen lamp heater and cooling the film naturally to room temperature. The as-grown Sb₂Se₃ films were cleaned with a deionized water rinse, and then graphite and Ag paste was screen printed on the Sb₂Se₃ (with an active area of 0.08 cm²), respectively, to define the solar cells.

Solar Cell Measurement: The finished solar cells current-voltage (J-V) curve were characterized using a solar simulator (Newport, Oriel Class AAA 94063A, 1000 Watt Xenon light source) with a source meter (Keithley 2420) at 100 mW cm⁻² AM 1.5G irradiation. A calibrated Si-reference cell and meter (Newport, 91150V, certificated by NREL) was used to calibrate the solar simulator prior to each measurement. The EQE data were obtained by a solar cell spectral response measurement system (QE-T, Enli Tecnology, Co. Ltd).

Materials Characterization: The film thickness was determined by the surface profilometer (Dektak II). The structure chacterization of the films was performed by an X-ray diffraction System (X'Pert). The film morphology and chemical composition were determined by the scanning electron microscope (SEM, JEOL 7000) with Energy-Dispersive Spectroscopy (EDS) attached to the SEM. The Raman experiments were conducted on a single stage Raman spectrometer with a solid-state laser (Horiba LabRam HR, 532 nm wavelength). The absorbance and transmittance spectra were measured using a UV–Vis spectrometer (Shimadzu UV-1800). The AFM and conductive AFM images were recorded on a grounded Sb₂Se₃ sample using an atomic force microscopy (AFM, Park XE70). The topography and current images were simultaneously recorded in contact mode using a Pt/Ir coated contact probe (ANSCM-PT from





AppNano, Inc.). The cantilever spring constant was about $3\,N\,m^{-1}$ and resonance frequency was $\approx\!60\,kHz.$

First-Principles Calculations: Atomistic, electronic structures, and optical properties were calculated using first-principles density functional theory (DFT)^[30,31] as implemented in the Vienna Ab initio Simulation Package (VASP)^[32]. The Perdew-Burke-Ernzerhof (PBE)^[33] form of exchange-correlation functional within the generalized gradient approximation (GGA)^[34] and a plane wave basis set with a 400 eV energy cutoff were employed for VASP calculations. As van der Waals interaction is present between neighboring $(Sb_4Se_6)_n$ ribbons, we adopted optB86-vdW non-local correlation functional that approximately accounts for dispersion interactions.^[35-37] The structural optimization and electronic relaxation were calculated using a Γ -centered Monkhorst-Pack^[38] k-point sampling grid of $12 \times 4 \times 4$. The maximal residual force of each atom is less than 0.02 eV A⁻¹ and the convergence criteria for electronic relaxation was set to 10^{-6} eV. As the DFT-GGA often underestimates the band gap, we adopt the modified Becke-Johnson (MBI) exchange potential^[39,40] and hybrid HSE06 functional^[41] for electronic structure and optical property calculations, a k-point grid of $28 \times 12 \times 12$ in the MBJ calculations, and a k-point grid of $9 \times 3 \times 3$ in the HSE06 calculations. The MBJ calculation yields a band gap close to that from the HSE06 caculation for Sb₂Se₃.

Supporting Information

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

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Conflict of Interest

The authors have declared no conflict of interest.

Keywords

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