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Ping Fan, Guo-Jie Chen, Shuo Chen, Zhuang-Hao Zheng, Muhammad Azam, et al.. Quasi-Vertically Oriented Sb(2)Se(3) Thin-Film Solar Cells with Open-Circuit Voltage Exceeding 500 mV Prepared via Close-Space Sublimation and Selenization. ACS Applied Materials & Interfaces, 2021, 13 (39), pp.46671-46680. 10.1021/acsami.1c13223 . hal-03369229

HAL Id: hal-03369229

<https://hal.science/hal-03369229>

Submitted on 15 Jun 2023

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Quasi-vertically oriented Sb₂Se₃ thin-film solar cell with open-circuit voltage exceeding 500 mV prepared via close-space sublimation and selenization

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Keywords: Sb₂Se₃; solar cell; orientation; open-circuit voltage; close-space sublimation

Abstract

Sb_2Se_3 , one of the most desirable absorption materials for next-generation thin-film solar cells, has an excellent photovoltaic characteristic. The $[\text{hk}1]$ -oriented (quasi-vertically oriented) Sb_2Se_3 thin film is more beneficial for promoting efficient carrier transport than the $[\text{hk}0]$ -oriented Sb_2Se_3 thin film. Controlling thin-film orientation remains the main obstacle to the further improvement in the efficiency of Sb_2Se_3 -based solar cells. In this work, the controlled $[\text{hk}0]$ or $[\text{hk}1]$ orientation of the Sb_2Se_3 precursor is readily adjusted by tuning the substrate temperature and the distance between the source and the sample in close-space sublimation (CSS). Well-crystallized stoichiometric Sb_2Se_3 thin films with the desired orientation and large crystal grains are successfully prepared after selenization. Sb_2Se_3 thin-film solar cells in a substrate configuration of glass/Mo/ Sb_2Se_3 /CdS/ITO/Ag are fabricated with a power conversion efficiency of 4.86% with a record open-circuit voltage (V_{OC}) of 509 mV. The significant improvement in V_{OC} is closely related to the quasi-vertically oriented Sb_2Se_3 absorber layer with reduced deep-level defect density in the bulk and defect passivation at the Sb_2Se_3 /CdS heterojunction. This work indicates that CSS and selenization show a remarkable potential for the fabrication of high-efficiency Sb_2Se_3 solar cells.

1. Introduction

Photovoltaic (PV) technology offers a safe, sustainable solution to the worsening global energy crisis by enabling the direct conversion of solar radiation into electricity.¹⁻³ Thin-film solar cells have the advantage of low cost, high efficiency, and improved device flexibility and are thus viable substitutes to Si-based solar cells. Solar cells based on CdTe and CuInGaSe have achieved the power conversion efficiency (PCE) values of 22.1% and 23.35%, respectively.⁴⁻⁷ However, their wide practical application is

considerably hindered by the toxicity of Cd and the scarcity of In and Te, which are used in both types of solar cells. Shockley–Queisser theory states that single-junction solar cells with a suitable bandgap ($E_g \approx 1.14$ eV) of the absorber material can exhibit the maximum PCE of 33.3%.⁸ Sb_2Se_3 thin-film solar cells have emerged as promising alternatives to other thin-film solar cells and exhibit great potential for low-cost and low-toxicity PV applications because of their attractive optoelectronic properties, such as suitable bandgap (1.1–1.3 eV), high absorption coefficient ($>10^5$ cm^{-1} in the visible wavelength region), decent carrier mobility, and stable binary compound composition.^{9–}

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Given that the PCE of Sb_2Se_3 thin-film solar cells can increase from 1.9% to 9.2%, Sb_2Se_3 is considered to be one of the most desirable photoactive materials for next-generation thin-film solar cells.^{9,11–18} However, a few drawbacks, such as open-circuit voltage (V_{OC}) loss and back contact barrier, require urgent solution to further improve the PCE of Sb_2Se_3 .¹⁹ The key prerequisite for promoting the PCE of Sb_2Se_3 thin-film solar cells is to enhance crystal quality by controlling the orientation of the Sb_2Se_3 layer. Sb_2Se_3 has a typical one-dimensional (1D) ribbon crystal structure that consists of nanobelts stacked along the x- and c-axes.²⁰ In the $[\text{hk}0]$ -orientation, the nanobelts are connected by van der Waals forces, whereas in the $[\text{hk}1]$ -orientation, the inside of the $(\text{Sb}_4\text{Se}_6)_n$ ribbons is covalently bonded via Sb–Se bonds along the c-axis.^{21–22} In addition, the bonds within the ribbons are stronger than those between the ribbons.² The difficult production of ion recombination centers at benign grain boundaries (GBs) implies that electrons are easy to transport in the band but are difficult to conduct between ribbons. Given the 1D structure, GBs parallel to the ribbons can be inherently beneficial for charge–carrier recombination.²³ Previous reports have indicated that $[\text{hk}1]$ -oriented Sb_2Se_3 thin films show improved PCE.²⁴ Moreover, the PCE of Sb_2Se_3

has been found to increase when the [211]-oriented Sb_2Se_3 thin films are more dominant than the [221]-orientated Sb_2Se_3 thin films.²⁵ The vapor transport deposition growth process is used to deposit Sb_2Se_3 films with preferential [211] and [221] orientations, which show higher PCE values than films with [020] and [120] orientations.²⁶ Mai's group fabricated high-quality Sb_2Se_3 thin films with [221] orientation on the CdS and Mo layers by co-evaporating Sb_2Se_3 and Se; the thin films show promising PCE.²⁷⁻²⁸ Therefore, controlling the preferred [hk1] orientation in Sb_2Se_3 layers is urgently needed to enhance carrier transport and extraction properties to improve PCE.

Generally, devices prepared through physical deposition methods show better device performance in PV applications than those prepared via chemical deposition methods. Close-space sublimation (CSS) is more widely used than other methods for the deposition of a variety of inorganic films, such as the binary compound CdTe, because of its fast processability and high efficiency. These characteristics make CSS a feasible method for industrial-scale manufacturing. Moreover, the film orientation of 1D Sb_2Se_3 is sensitive to temperature. According to Fan's early work, CSS is a highly promising method for Sb_2Se_3 film deposition because it not only produces large grains with the preferred orientation but is beneficial for controlling grain structure.^{17-18,29} Mai's group fabricated high-quality Sb_2Se_3 nanorod array solar cells with core-shell structure and efficiency reaching 9.2%.⁹ The nanorod arrays along the [hk1]-orientation are highly conducive to light absorption and charge carrier extraction. Despite such advantages, the nanorod arrays have a rough surface that easily leads to electric leakage and large V_{OC} deficit⁹ likely because the vapor pressure of Se is significantly greater than that of Sb during sublimation; furthermore, the reduction in device performance is attributed to Se vacancies originating from the loss of Se.³⁰⁻³¹ Therefore, we need to explore a new strategy to improve the film quality and device performance of Sb_2Se_3 solar cells. Our

group previously reported on the deposition of high-quality Sb_2Se_3 thin films with a high V_{OC} of 504 mV via a two-step process involving the radiofrequency magnetron sputtering deposition of amorphous Sb_2Se_3 followed by post-selenization.¹⁴ In this work, we obtained [hk1]-oriented Sb_2Se_3 thin-film solar cells through CSS followed by post-selenization. Notably, the V_{OC} of our champion device reached 509 mV, which is higher than that of any other reported Sb_2Se_3 thin-film solar cell in the literature.^{9,11,14} Our work provides an effective method for manufacturing highly efficient Sb_2Se_3 solar cells.

2. Experimental detail

2.1. Preparation of Sb_2Se_3 thin films

First, soda-lime glass (SLG) substrates were ultrasonically cleaned with detergent, deionized water, isopropanol, ethanol, and deionized water for 20 min. A Mo thin film with a thickness of approximately 1 μm was sputtered on the SLG substrate via magnetron sputtering. The schematic of the preparation process of the Sb_2Se_3 thin film is provided in **Fig. 1**. Mai's group fabricated Sb_2Se_3 nanorod arrays via CSS,⁹ whereas we obtained large Sb_2Se_3 grains by performing an additional post-selenization process. The substrate temperature ($T_{\text{substrate}}$) was controlled by using a ceramic light visor inserted between the source and substrate to prevent the overheating of the graphite substrate holder by interactive light radiation. High-purity (>99.99%) Sb_2Se_3 powder was compressed in a graphite box. The distance between the source and the sample holder was 9 mm. The pressure of the vacuum chamber was kept below 0.6 Pa prior to deposition. For sublimation, first, $T_{\text{substrate}}$ and source temperature (T_{source}) were kept at 290 °C for 2 min. Subsequently, T_{source} was gradually increased from 290 °C to ≈ 300 °C and then to 510 °C for 2 min. The whole sublimation process was completed in 10 min.

The graphite box was naturally cooled down to room temperature when the process was completed. As shown in **Fig. 1**, the as-deposited Sb_2Se_3 thin films and 0.2 g of the high-purity Se powder (99.999%) were placed into a double-chamber vacuum tubular furnace. The distance between the Se powder and the sample is 23 cm, and the diameter of the pipe is 50 mm. The chambers were evacuated by using a mechanical pump, and then high-purity argon gas (>99.999%) was introduced to clarify the chambers exhaustively before selenization. A sufficient Se pressure was provided with a high working pressure of 5×10^4 Pa to passivate the Se vacancy and obtain a suitable composition. The Se powder side and the Sb_2Se_3 thin film side was simultaneously heated to 400 °C and 420 °C for 15 min, respectively. Herein, Sb_2Se_3 thin films with different orientations were obtained by exactly controlling $T_{\text{substrate}}$ and T_{source} . The samples deposited at different $T_{\text{substrate}}$ and T_{source} were denoted as S1 ($T_{\text{substrate}} = 260$ °C and $T_{\text{source}} = 520$ °C), S2 ($T_{\text{substrate}} = 260$ °C and $T_{\text{source}} = 510$ °C), S3 ($T_{\text{substrate}} = 290$ °C and $T_{\text{source}} = 510$ °C), and S4 ($T_{\text{substrate}} = 270$ °C and $T_{\text{source}} = 520$ °C) and denoted as SS1, SS2, SS3, and SS4, respectively, following post-selenization.

2.2. Fabrication of Sb_2Se_3 thin-film solar cells

After deposition and selenization, the CdS buffer layer was deposited on the Sb_2Se_3 thin films through chemical bath deposition. CdSO_4 aqueous solution (0.015 M), thiourea aqueous solution (0.75 M), and ammonium hydroxide aqueous solution were subsequently added to the deionized water. The Sb_2Se_3 thin films were immersed in the mixed solution and then placed in a water bath at 80 °C under continuous stirring for 9 min. After that, the substrates were rinsed with deionized water and dried in an oven. An ITO window layer was subsequently deposited via magnetron sputtering for 25 min at a power of 110 W and a pressure of 0.4 Pa. Finally, the device surface was scored

into small squares with an identical area of 0.16 cm^2 by using a knife, and Ag electrodes were deposited as the metallic contact onto the ITO surface by using thermal evaporation.

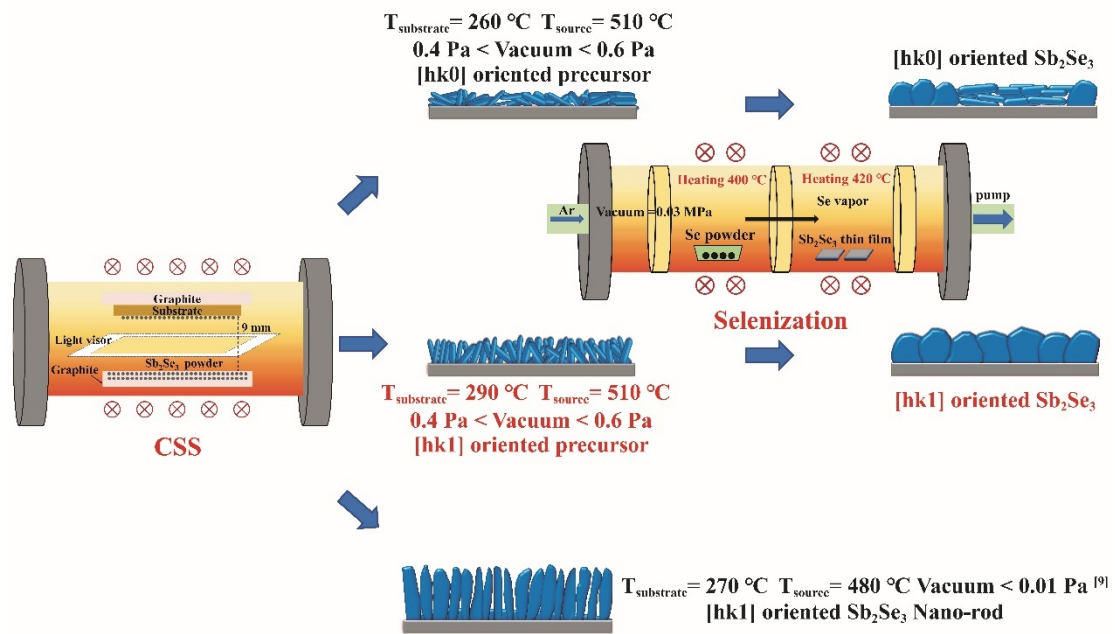


Fig. 1. Schematic illustration of the close-spaced sublimated and selenized Sb_2Se_3 thin-film.

2.3. Characterizations

We analyzed the Sb_2Se_3 thin films by using various techniques to determine the effect of temperature on the orientation of film growth and the PCE of the devices. The crystal orientation of the Sb_2Se_3 thin films was characterized by applying X-ray diffraction (XRD, Ultima-iv) with $\text{CuK}\alpha$ radiation under the operation conditions of 40 kV and 40 mA from 10° to 60° . Raman spectra were obtained with an excitation wavelength of 532 nm. The surface and cross-sectional morphologies of the thin films were observed with a thermal field-emission scanning electron microscope (SEM, Zeiss SUPRA 55), and the chemical compositions and elemental distribution of the film were analyzed by using a SEM-coupled energy-dispersive X-ray spectroscope (EDS, BRUKER

QUANTX 200). The current density–voltage (J–V) curves of the Sb₂Se₃ devices were recorded by using a multimeter (Keithley, 2400 Series) under 100 mW/cm² AM 1.5 G light illumination at room temperature. External quantum efficiency (EQE) spectra were acquired by using a Zolix SCS101 system and a Keithley 2400 source meter. Capacitance–voltage (C–V) measurements were obtained at an AC amplitude of 30 mV and a frequency of 10 kHz under dark conditions at room temperature. During C–V measurement, the DC bias voltage was applied from –1 V to 0.3 V. Drive-level capacitance profiling (DLCP) measurements were performed with an AC amplitude from 20 mV to 140 mV and a DC bias voltage from –0.2 V to 0.2 V. Temperature-dependent V_{OC} measurements were conducted by using a Lakeshore 325 temperature controller, and the temperatures were swept from 340 K to 160 K in a step of 20 K. Electrochemical impedance spectroscopy (EIS) was conducted by using a CHI600E Electrochemical Workstation. Temperature-dependent capacitance–frequency measurements were performed in the dark with varying temperatures within the range of 210 to 325 K with a 5 K step by using an Agilent 4284A LCR meter. The samples were mounted in a cryostat (Janis Ltd. CCS-150) and cooled with liquid He.

3. Results and discussion

XRD measurements were utilized to analyze the crystal orientation and crystallinity of the Sb₂Se₃ thin films. The XRD patterns are shown in **Fig. 2a** and **2d**. All the diffraction peaks were in good agreement with the information provided by the JCPDS standard card (No. 15–0861) of Sb₂Se₃ without any detectable impurities. The films showed different preferred orientations at various T_{substrate}. Importantly, the [hk0] peak intensities increased when the T_{substrate} was less than 270 °C. Previous works have shown that film orientation plays an important role in controlling carrier transport.¹¹

The texture coefficient (TC) of the diffraction peaks was calculated on the basis of the following equations to investigate the orientations of the Sb_2Se_3 thin films quantitatively:²⁴

$$TC(hkl) = \frac{I(hkl)}{I_0(hkl)} / \left(\frac{1}{N} \sum_{i=1}^N \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \right), \quad (1)$$

where $I(hkl)$ and $I_0(hkl)$ are the diffraction peak intensities of the $[hkl]$ planes in the measured and standard XRD pattern of Sb_2Se_3 (JCPDS 15–0861), respectively. The high TC of a diffraction peak demonstrates a preferred orientation and an increase in packing density along this designated direction.^{24,32} The TC values of the $[hk0]$ series of our sample decreased when the $T_{\text{substrate}}$ was increased from 260 °C to 290 °C during sublimation. By contrast, the TC value of the $[hk1]$ and $[hk2]$ planes stacked vertically on the substrate demonstrated the opposite trend, indicating that a high $T_{\text{substrate}}$ of 290 °C was suitable for the $[hk1]$ orientation of the films. The samples were characterized through Raman spectroscopy for the phase analysis of the Sb_2Se_3 absorber layer and further understanding. As shown in **Fig. 2c** and **2f**, all the as-deposited films exhibited three Raman peaks at 189 and 210 cm^{-1} , which were assigned to the Sb–Se vibration in the Sb_2Se_3 pyramidal unit, and a tiny peak at 253 cm^{-1} that could be attributed to the Se–Se bond.³³ The small peaks at 253 cm^{-1} indicated that amorphous Se was present in the as-deposited films.³³⁻³⁴ After post-selenization treatment, the small peaks disappeared likely because of the transformation of amorphous Se into the crystalline phase.³⁴ Raman spectroscopy revealed that no impurity phase was present in the Sb_2Se_3 thin film.

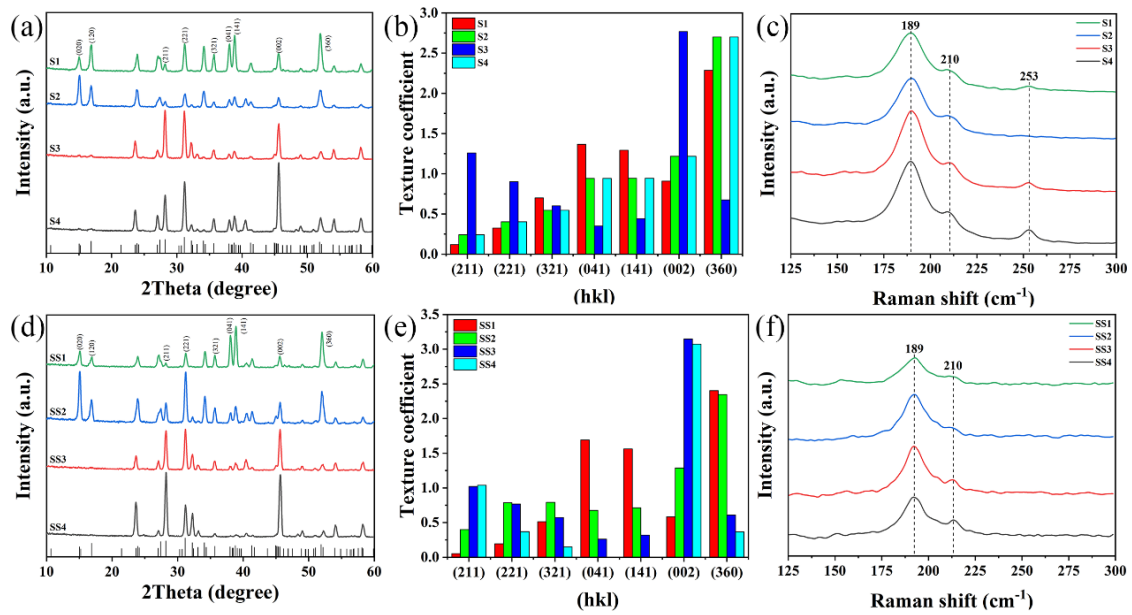


Fig. 2. (a) XRD patterns of Sb_2Se_3 thin-films with $T_{\text{substrate}}=260\text{ }^\circ\text{C}$ and $T_{\text{source}}=520\text{ }^\circ\text{C}$ (S1), $T_{\text{substrate}}=260\text{ }^\circ\text{C}$ and $T_{\text{source}}=510\text{ }^\circ\text{C}$ (S2), $T_{\text{substrate}}=290\text{ }^\circ\text{C}$ and $T_{\text{source}}=510\text{ }^\circ\text{C}$ (S3), $T_{\text{substrate}}=270\text{ }^\circ\text{C}$ and $T_{\text{source}}=510\text{ }^\circ\text{C}$ (S4), respectively. (b) Texture coefficient of Sb_2Se_3 thin-films with different temperature (S1, S2, S3 and S4). (c) Raman spectroscopy of different precursor Sb_2Se_3 thin-films. XRD patterns (d), Texture coefficients (e) and Raman spectroscopy (f) of the Sb_2Se_3 thin-films with a post-selenization treatment, which denoted as SS1, SS2, SS3, and SS4, respectively.

Fig. 3 and **Fig. 4** present the morphology, cross-sectional SEM images, and water contact angle of the Sb_2Se_3 thin films. The morphology of the Sb_2Se_3 films was studied via SEM as shown in **Fig. 3a** and **3c**. The surface SEM images of the as-deposited Sb_2Se_3 films were similar to those of the nanosheets with $[\text{hk}0]$ orientation as highlighted by a yellow dotted oval. However, after post-selenization treatment, highly crystallized Sb_2Se_3 films with $[\text{hk}0]$ orientation could be observed on the surface. This observation indicated that post-selenization treatment could increase the degree of crystallinity (**Fig. 3b** and **3d**). Furthermore, the $[\text{hk}0]$ orientation could be observed in the cross-sectional SEM image of the SS2 device in **Fig. 3f**. In contrast to **Fig. 3**, dense

nanosheets without pinholes could be observed in **Fig. 4**. With the increase in $T_{\text{substrate}}$, large crystals could be observed on the surfaces of the nanosheets in **Fig. 4b** and **4d** and grain size reached approximately $1.5 \mu\text{m}$, indicating that high $T_{\text{substrate}}$ during sublimation and the subsequent post-selenization treatment led to large grain sizes with the preferred $[hk1]$ orientation.^{31,35} Large grains are likely more beneficial for carrier transport than Sb_2Se_3 nanorod arrays.⁹ We assumed that heterojunction quality could be influenced by the chemical interaction between the CdS buffer layer and the Sb_2Se_3 absorber layer. We measured the water contact angles of the SS2 and SS3 thin films (**Fig. 3e** and **Fig. 4e**, respectively). The water contact angles of the SS3 and SS2 thin films were 32.91° and 82.66° , respectively. These results indicated that the increased hydrophilic characteristics of SS3 relative to those of SS2 favored CdS infiltration, which may improve $\text{Sb}_2\text{Se}_3/\text{CdS}$ heterojunction quality.

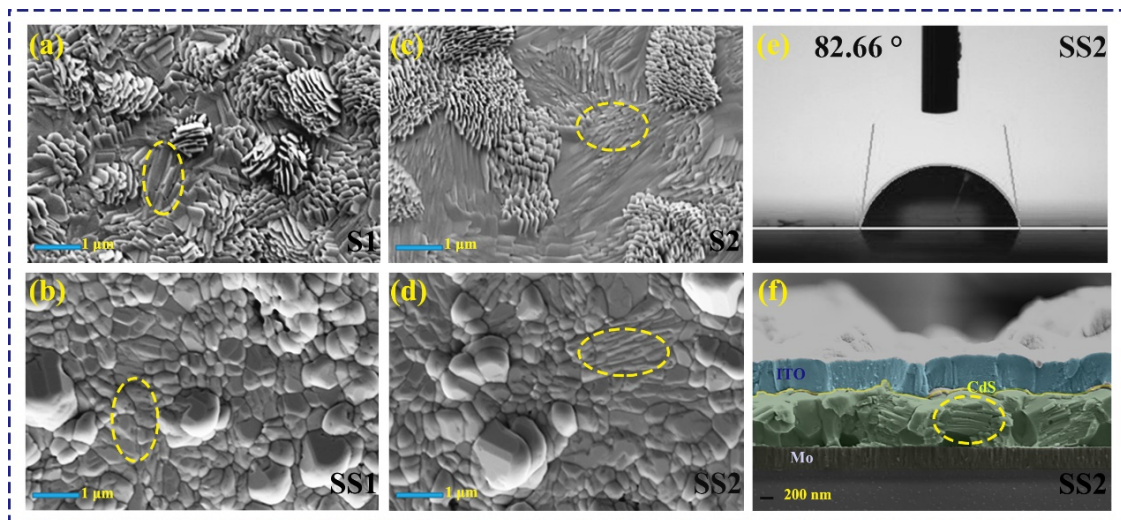


Fig. 3. Morphology evolution of Sb_2Se_3 thin-film. The morphology of Sb_2Se_3 thin-films without and with selenization for S1 (a), SS1 (b), S2 (c), SS2 (d). (e) The water contact angles for the SS2 thin-film. (f) Cross-sectional SEM image for the SS2 thin-film (final device).

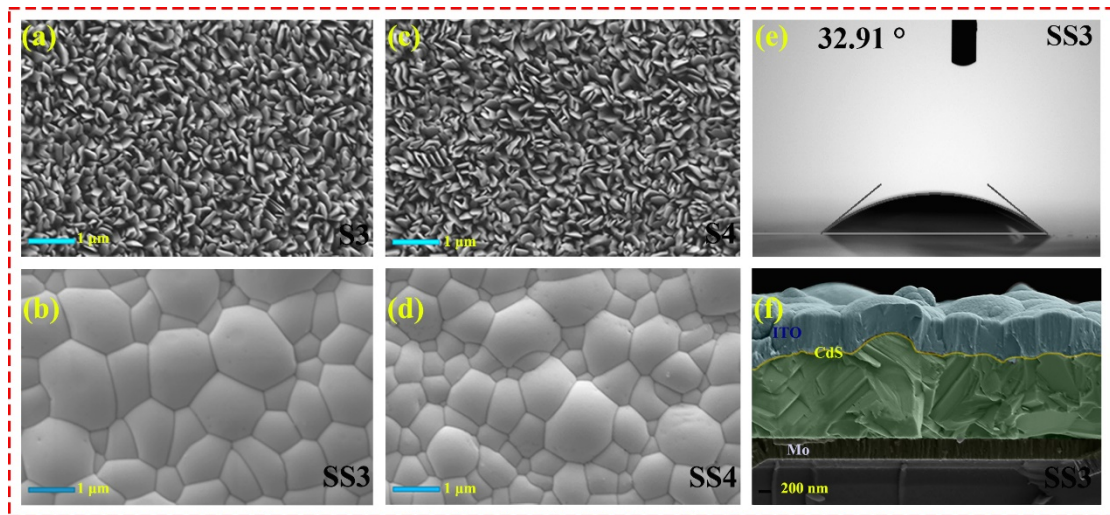


Fig. 4. Morphology evolution of Sb_2Se_3 thin-film. The morphology of Sb_2Se_3 thin-films without and with selenization for S3 (a), SS3 (b), S4 (c), SS4 (d). (e) The water contact angles for the SS3 thin-film. (f) Cross-sectional SEM image for the SS3 thin-film (final device).

An EDS platform equipped with the SEM system was used to characterize the chemical composition of the Sb_2Se_3 thin films. The chemical compositions of the as-deposited Sb_2Se_3 films and selenized films are shown in **Table 1**. The Se content of all the as-deposited Sb_2Se_3 precursor thin films was relatively low. Therefore, through the post-selenization treatment of Sb_2Se_3 thin films, the Se vacancy defects in the Sb_2Se_3 absorption layer could possibly be reduced during sublimation, thus leading to the recombination suppression of the device. The Se ratios of all the selenized Sb_2Se_3 thin films increased. Furthermore, post-selenization treatment could lead to sufficient crystallization, which can reduce interface and bulk defect densities.

Table 1 The chemical composition of the Sb_2Se_3 thin-films deposited at different $T_{\text{substrate}}$ and T_{source} by CSS with and without selenization

Sample	Sb (at. %)	Se (at. %)	Sb/Se ratio
S1	40.67	59.33	0.68
S2	41.27	58.73	0.70
S3	40.36	59.64	0.67
S4	42.33	57.67	0.73
SS1	40.27	59.73	0.67
SS2	38.22	61.78	0.62
SS3	39.16	60.84	0.64
SS4	38.11	61.89	0.62

After fabricating the Sb_2Se_3 absorber layer, CdS, ITO, and the front electrode were sequentially fabricated to obtain a device with a substrate configuration of SLG/Mo/ Sb_2Se_3 /CdS/ITO/Ag. The cross-sectional SEM images of the actual devices (SS2 and SS3) are shown in **Fig. 3f** and **Fig. 4f**. As expected, large Sb_2Se_3 grains of the SS3 device penetrated through the whole absorber layer, making it suitable for the transport and extraction of photogenerated carriers. But for the SS2 device, the layered Sb_2Se_3 with the [hk0] orientation can be found in **Fig. 3f**. Overall, when the as-deposited Sb_2Se_3 precursor films exhibiting nanosheets with [hk1] orientation, high crystallinity with [hk1] preferred orientation could be obtained via the post-selenization process, which is essential for carrier transport to enhance the V_{OC} .³¹

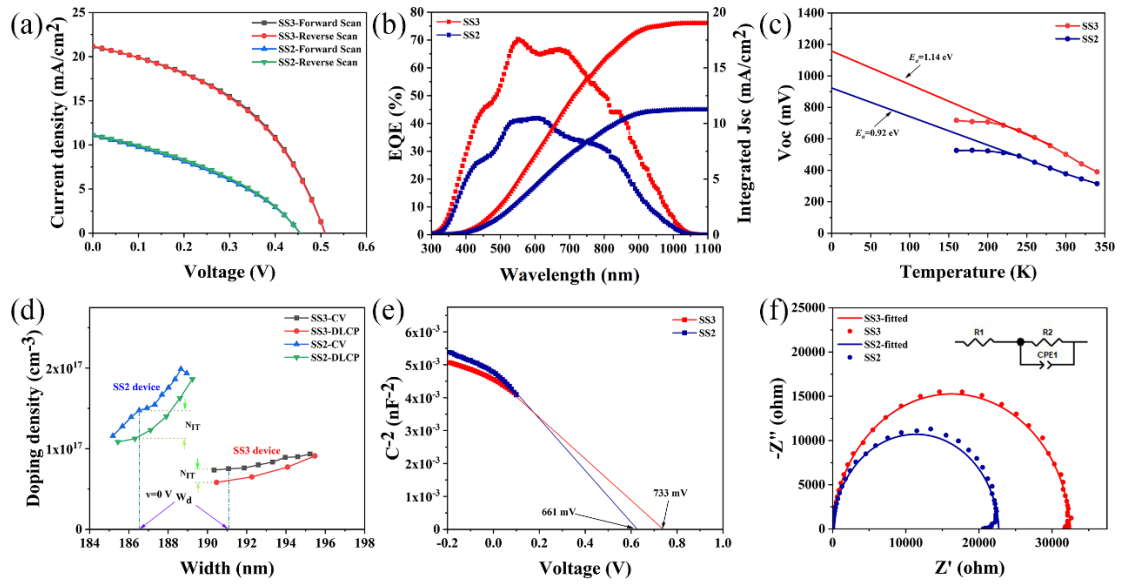


Fig. 5. Device performance characterizations of the Sb₂Se₃ solar cells. (a) The J-V of the SS2 and SS3 devices with different scanning directions. (b) EQE and the integrated J_{sc} of SS2 and SS3 devices. (c) Temperature dependent V_{oc} measurement, (d) C-V profiling and DLCP measurement, (e) 1/C²-V curves and (f) electrochemical impedance spectroscopies of the SS2 and SS3 devices.

The J-V curves of the Sb₂Se₃ solar cells were obtained under AM 1.5 G light illumination with different scanning directions as shown in **Fig. 5a**. Notably, in both devices, the hysteresis effect was negligible as reflected by the nearly overlapping J-V curves in the forward and reverse scan directions. The detailed PV parameters and the statistical distribution are summarized in **Fig. 6.** and **Table 2.** Most of the SS3 devices presented a high V_{oc}, indicating that the stability and reproducibility of this trend is good. The J-V measurement indicated that the SS2 device demonstrated a PCE of 1.94% with a V_{oc} of 453 mV, short circuit current density (J_{sc}) of 11.47 mA/cm², and fill factor (FF) of 37.32%. By contrast, the SS3 device showed a significant increase in PCE to 4.86% with the corresponding enhancement in V_{oc} to 509 mV, J_{sc} to 21.15 mA/cm², and FF to 45.10%. This result indicated that increasing the T_{substrate} induced

the preferred orientation of the film and further yielded devices with improved efficiencies.^{26,36} As shown in **Table 3**, the lower FF value of our device than that of the other devices fabricated via other methods might be ascribed to degradation in the junction and absorber layer quality. The V_{OC} values of the SS2 and SS3 devices were 453 and 509 mV, respectively, which were higher than those of most high-efficiency Sb_2Se_3 solar cells.^{9,11}

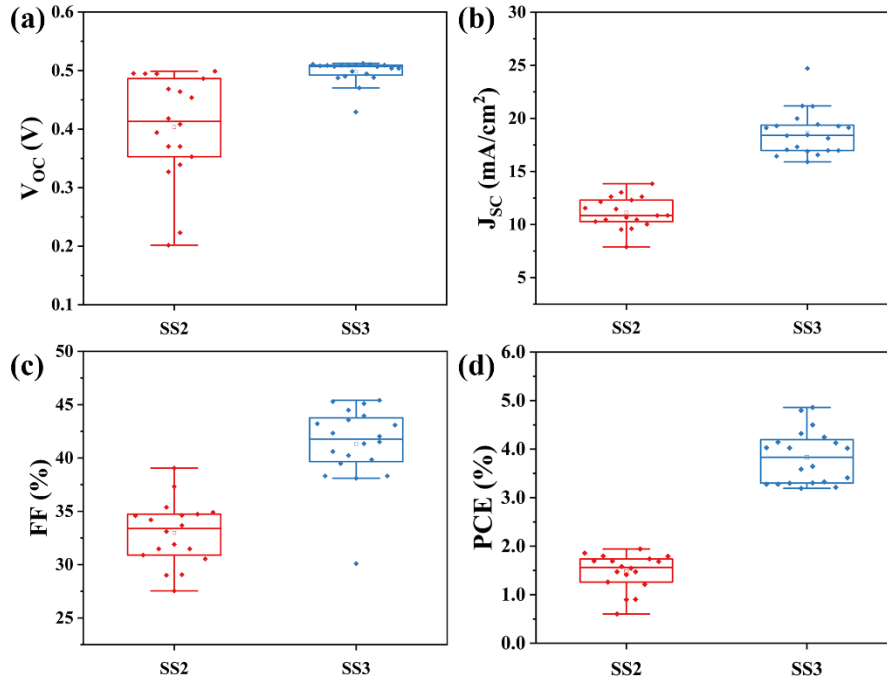


Fig. 6. Statistical distribution of the device performance parameters including (a) open-circuit voltage (V_{OC}), (b) short-circuit current density (J_{SC}), (c) fill factor (FF) and (d) power conversion efficiency (PCE).

Table 2 Device parameters of the Sb_2Se_3 solar cells fabricated under different temperature

Samples	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF (%)	Eff (%)
SS3	509	21.15	45.10	4.86
SS2	453	11.47	37.32	1.94

Table 3 Comparison of device characterize of planer heterojunction Sb_2Se_3 solar cells

via different fabrication methods

Method	Device configuration	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	Eff (%)	Ref.
CSS ^a	Mo/Sb ₂ Se ₃ /Cd _x Zn _{1-x} S/ZnO/AZO	403	25.69	64.78	6.71	Mai ³⁷
CSS ^a	SLG/Mo/MoSe ₂ /NA-Sb ₂ Se ₃ /TiO ₂ /CdS/ZnO/Al:ZnO	400	32.58	70.3	9.2	Mai ⁹
Co-eva ^b	Mo/Sb ₂ Se ₃ /CdS/ ZnO/AZO/Ag	427	17.11	58.15	4.25	Mai ²⁸
Sput-Se ^c	Mo/Sb ₂ Se ₃ /CdS/ ITO/Ag	494	25.91	47.7	6.06	Our work ¹³
Sput-Sb-Se ^d	Mo/Sb ₂ Se ₃ /CdS/ ITO/Ag	504	24.91	54.47	6.84	Our work ¹⁴
CSS-Se ^e	Mo/Sb ₂ Se ₃ /CdS/ ITO/Ag	509	21.15	45.10	4.86	This work

a Closed space sublimation.

b Co-evaporation.

c Sputtering Sb₂Se₃ and post-selenization.

d Sputtering Sb precursor and post-selenization.

e Closed space sublimation Sb₂Se₃ and post-selenization.

The EQE of the SS2 and SS3 devices are presented in **Fig. 5b**. The EQE spectrum of the SS3 device demonstrated a higher photoresponse from 300 nm to 1100 nm than that of the SS2 device. The maximum EQE of the SS3 device was close to 70% at approximately 550 nm, whereas the maximum EQE value of the SS2 device was less than 45% from 300 nm to 1100 nm, indicating that the performance of the SS3 device was considerably better than that of the SS2 device. The reduction in photoresponse was related to undesirable film orientation and thus short electron diffusion length, resulting in lower J_{sc}. The electron diffusion length along the [hk1]-oriented grains, which indicated a reduction in dangling bonds and recombination centers at GBs, can reach a high level.²⁶ However, due to the weak interactions between (Sb₄Se₆)_n ribbons, electrons are difficult to transport in the [hk0]-oriented grains. Further, the EQE values of Sb₂Se₃ sharply declined from 800 nm to 1100 nm due to the insufficient generation and collection of the carriers leading to a low J_{sc}.³¹ Moreover, when the [211]

preferentially oriented films were more dominant than the [221] preferentially oriented films, the efficiency of Sb_2Se_3 increased.²⁵ The integrated J_{SC} values of the SS2 and SS3 devices calculated from EQE data were 18.98 and 11.22 mA/cm^2 , respectively, which were in good agreement with the values obtained from J–V measurements.

Temperature-dependent V_{OC} measurement was carried out to characterize the carrier transport behavior from 340 K to 140 K and to further analyze interface characteristics.

As shown in **Fig. 5c**, the activation energy (E_a) of the dominant recombination within the devices could be calculated by extrapolating the V_{OC} curves to the Y-axis.¹³ The E_a of the SS3 device was 1.14 eV, which was very close to the band gap of Sb_2Se_3 (1.20 eV), whereas that of the SS2 device was only 0.92 eV. This result implied that interfacial recombination was more prominent for the SS2 device than for the SS3 device mainly due to poor adhesion at the $\text{Sb}_2\text{Se}_3/\text{CdS}$ interface originating from dangling-bond-rich GBs of the SS2 device.¹³

C–V profiling and DLCP measurements were performed to investigate the interfacial defects of the devices, and the results are shown in **Fig. 5d**. In previous literature,¹¹ the doping density $N_{\text{C-V}}$ measured by the C–V includes free carriers, bulk defects, and interfacial defects, whereas the DLCP-measured doping density N_{DLCP} only includes free carriers and bulk defects.¹³ Hence, the interfacial defects of the device could be calculated via $N_{\text{C-V}} - N_{\text{DLCP}}$. The plots of $N_{\text{C-V}}$ and N_{DLCP} against the profiling width x can be obtained in accordance with the following equations:³⁸

$$\left\{ \begin{array}{l} N_{\text{C-V}} = \frac{-2\varepsilon_r n N_D}{\left(\frac{d\left(\frac{1}{C^2}\right)}{dV}\right) q A^2 \varepsilon_0 \varepsilon_r n \varepsilon_r p N_D + 2\varepsilon_r p}, \\ N_{\text{DLCP}} = -\frac{C_0^3}{2q \varepsilon_0 \varepsilon_r p A^2 C_1}, \\ x = \frac{\varepsilon_0 \varepsilon_r p A}{C_0}, \end{array} \right. \quad (2)$$

where N_D is the doping density of CdS; A is the device area; $\epsilon_{r,n}$ and $\epsilon_{r,p}$ are the relative permittivity of CdS and Sb_2Se_3 , respectively; and C_0 and C_1 are two quadratic fitting parameters derived from the $C-V$ curves. Considering that DLCP is a purely dynamic measurement and deep defects might affect the depletion width (X_d), we used the same x-axis, which represented the distance from the Sb_2Se_3/CdS interface, for both curves (**Fig. 5d**). The gap between the DLCP and $C-V$ profiling curves of the SS2 device was large, whereas the discrepancy between both curves of SS3 device was considerably small, implying low defect density and recombination loss at the Sb_2Se_3/CdS interface. The interface defect densities ($N_{C-V} - N_{DLCP}$ at zero bias) for the SS2 and SS3 devices were calculated as 3.504×10^{16} and $1.689 \times 10^{16} \text{ cm}^{-3}$ respectively, indicating that a desirable orientation could enhance the quality of the Sb_2Se_3 absorber. Moreover, the values of N_{DLCP} for the SS2 device and SS3 device were 1.13×10^{17} and $5.83 \times 10^{16} \text{ cm}^{-3}$, respectively. Furthermore, if the carrier concentration was assumed to be constant, then the SS3 device exhibited a lower defect than the SS2 device. This result was supported by the characterization of the morphology of the precursor Sb_2Se_3 thin films (**Fig. 3** and **4**). In addition, the X_d of the SS3 device was longer than that of the SS2 device, and the interfacial defects originated from dangling-bond-rich GBs would be passivated,^{14,17} resulting in reduced defect density and recombination loss. This reduction could account for the higher J_{SC} of the SS3 device than that of SS2 device.

Fig. 5e shows the $1/C^2-V$ curves. The heterojunction-dependent built-in voltage (V_{bi}) of the device could be inferred from the X-axis intercept of the $C-V$ profiling curves. The V_{bi} value of the SS2 and SS3 devices were 661 and 773 mV, respectively. The difference in V_{bi} could be attributed to the enhanced built-in-electric field, improved Sb_2Se_3/CdS interface, and large grain size obtained via the post-selenization process, leading to the remarkable increase in the V_{OC} of our best device. EIS measurements

were also acquired to analyze the interfacial charge transfer properties of the device. **Fig. 5f** presents the Nyquist plots of the impedance spectra of the different devices, and the equivalent circuit model that was utilized to fit the impedance curves is shown in the inset. The recombination resistance (R_s) values of the SS2 and SS3 devices were directly obtained from the arc's diameter length and were 22714 and 32419 Ω , respectively. Our best device (SS3) exhibited high recombination resistance, which restrained the charge recombination at the $\text{Sb}_2\text{Se}_3/\text{CdS}$ interface and was responsible for the enhancement in V_{OC} .

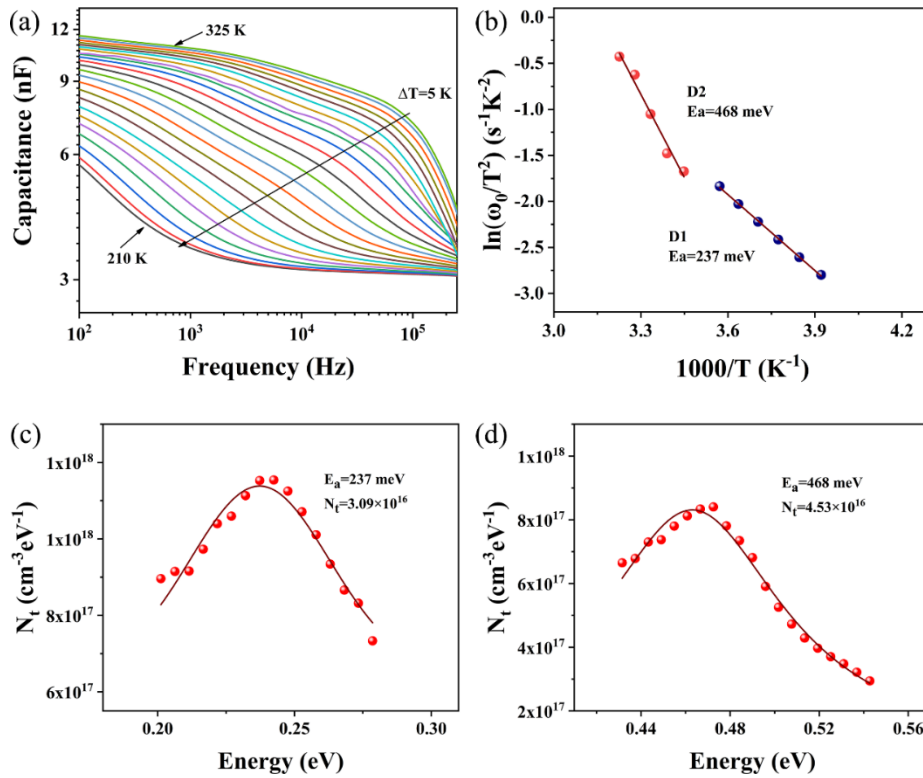


Fig. 7. Temperature-dependent admittance results for the champion SS3 device. (a) Capacitance-frequency-temperature (C-f-T) spectra (b) the Arrhenius plots of ω_0/T^2 versus $1000/T$ for two defects; the defect activation energies (E_a) were calculated for each defect and are shown inside the figure. Defect density of D1 (c) and D2 (d) derived from the admittance spectra.

Admittance spectroscopy measurements, which are usually utilized to speculate the energy level of defects inside the band gap, were acquired to gain a further understanding of the distribution and density of defects in the Sb₂Se₃ device.³⁹ Although admittance spectroscopy involves measuring conductance and capacitance as a function of angular frequency (ω) and temperature (T),

$$Y(\omega, T) = i\omega C(\omega, T) + G(\omega, T), \quad (3)$$

which is the measurement of complex admittance, only capacitance spectra $C(\omega, T)$ are usually discussed.⁴⁰ As illustrated in **Fig. 7a**, the capacitance–frequency (C–f) spectra were obtained over the temperature range of 210 K to 325 K with steps of 5 K and the frequency range of 100 Hz to 1 MHz. Two capacitance steps were obviously distinguishable with different frequencies. These steps could be described as two different defect levels, which were denoted as D1 and D2. The inflection frequencies ($\omega_0 = 2\pi f_0$) corresponding to the admittance spectrum were derived from the angular frequency point ω at the maximum of the $\omega dC/d\omega$ vs. ω plot. Defect activation energies (E_a) were derived from the slopes of the Arrhenius plots that were linearly fitted based on the following equation:⁴¹⁻⁴³

$$\omega_0 = 2\pi\nu_0 T^2 \exp\left(\frac{-E_a}{kT}\right), \quad (4)$$

where ν_0 is the attempt-to-escape frequency; ω_0 is the inflection point frequency; k is the Boltzmann constant; and E_a is the defect activation energy, representing the average defect energy level relative to the valence band maximum or conduction band minimum. In accordance with the theoretical results obtained through first-principles calculation, the intrinsic defects belonging to Sb₂Se₃ could be approximately described as Sb antisite (Sb_{se}) and Se vacancy (V_{se}).^{30,44} As shown in **Fig. 7b**, D1 could roughly be ascribed to V_{se} vacancy defects with a low E_a of 237 meV, whereas D2 could roughly be ascribed to Sb_{se} antisite defects with a high E_a of 468 meV.⁴⁵ For the further

evaluation of the defects, the distribution of each defect type was Gaussian-fitted by using the Kimerling model based on the following equations:⁴⁶

$$E(\omega) = kT \ln\left(\frac{2\pi\nu_0 T^2}{\omega}\right), \quad (5)$$

$$N_t(E(\omega)) = -\frac{V_d}{q\omega} \frac{dC}{d\omega} \frac{\omega}{kT}, \quad (6)$$

where V_d is the built-in potential of the p-n junction, ω is the angular frequency, and $N_t(E[\omega])$ is the defect density. The defect densities of different E_a are shown in **Fig. 7c** and **d**. The defect densities of the SS3 device were 3.09×10^{16} and $4.53 \times 10^{16} \text{ cm}^{-3}$, respectively. These results were almost one order of magnitude higher than the results for a previously reported high-efficiency device likely because the abundance of defects acted as recombination centers, producing recombination losses in the absorber layer and the heterojunction interface that further impaired device performance. In short, with respect to the above discussion, we found that a high-quality absorber layer with the few defects is extremely crucial to the high-performance device.

4. Conclusion

High-quality Sb_2Se_3 films were deposited via the CSS method and subjected to post-selenization treatment. $T_{\text{substrate}}$ significantly influenced the orientation of the precursor films. With the precise control of the $T_{\text{substrate}}$ and the suitable distance between the source and the sample, the Sb_2Se_3 precursor in the preferred quasi-vertical orientation was prepared with the $T_{\text{substrate}}$ and distance of 290 °C and 9 mm, respectively. After selenization, highly crystallized Sb_2Se_3 films in the optimal orientation, which was essential for improving device performance, were obtained. A Sb_2Se_3 thin-film solar cell with a PCE of 4.86% was successfully assembled owing to this orientation control

strategy. Notably, our cell demonstrated the record V_{OC} of 509 mV, which was closely related to deep-level defect suppression in the bulk film and defect passivation at the Sb_2Se_3/CdS heterojunction. Our effective orientation-controlling strategy via CSS and post-selenization treatment shows a remarkable potential for the further performance improvement of Sb_2Se_3 solar cells.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 62074102), Key Project of Department of Education of Guangdong Province (No. 2018KZDXM059), Science and Technology plan project of Shenzhen (JCYJ20190808153409238 and 20200812000347001) and Natural Science Foundation of Guangdong Province (2020A1515010805)

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