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# Spark plasma sintering of Sb<sub>2</sub>Se<sub>3</sub> sputtering target towards highly efficient thin film solar cells

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**ABSTRACT:** Antimony selenide (Sb<sub>2</sub>Se<sub>3</sub>) is a potential absorber material for environment-friendly and cost-efficiently photovoltaics due to its material advantages and superior optoelectronic properties. In this work, we proposed a facile and versatile method of ball milling followed with spark plasma sintering (SPS) to prepare high-quality Sb<sub>2</sub>Se<sub>3</sub> sputtering target. Then the highly crystalline Sb<sub>2</sub>Se<sub>3</sub> thin film consisted of large crystal grains can be prepared by using radio frequency (RF) magnetron sputtering with an additional post-selenization heat treatment. An efficient substrate structured Sb<sub>2</sub>Se<sub>3</sub> thin film solar cell with configuration of Mo/Sb<sub>2</sub>Se<sub>3</sub>/CdS/ITO/Ag was fabricated and a champion device with highly interesting power conversion efficiency (PCE) of 5.08% has been achieved. Superior device performances are closely related to the Sb<sub>2</sub>Se<sub>3</sub> absorber layer with benign growth orientation and the Sb<sub>2</sub>Se<sub>3</sub>/CdS heterojunction interface with smooth contact, which induced less recombination loss. The combined features of homemade sputtering target and advantageous thin film preparation technology further demonstrated its attractive application potential in thin film photovoltaic scenarios.

**KEYWORDS:** Sb<sub>2</sub>Se<sub>3</sub>, sputtering target, spark plasma sintering, magnetron sputtering, post-selenization, thin film solar cells

# 1. Introduction

Solar cells which can directly convert solar energy into electric power have drawn tremendous research attentions because of the potential to partially compensate the non-renewable fossil fuels.<sup>[1-3]</sup> Among various kinds of solar cells, silicon-based series, copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) thin films are the dominant materials currently used in photovoltaic scenarios and all of them have achieved certified power conversion efficiency (PCE) higher than 20%.<sup>[4-7]</sup> However, the intrinsic indirect band gap and a relatively low absorption coefficient of Si requires a thick wafer to absorb sunlight, which still costs more than traditional fuels in power production.<sup>[4]</sup> The natural scarcity of Te, In and Ga on Earth, as well as the toxicity of Cd are the main concerns for CIGS and CdTe solar cells.<sup>[8]</sup> Thus, alternative environment-friendly and cost-efficiently photovoltaic materials are urgently required and actively investigated. The binary semiconductor of antimony selenide (Sb<sub>2</sub>Se<sub>3</sub>) can be considered as a promising candidate because of its attractive optoelectronic properties, such as an appropriate band gap (1.1-1.3 eV, approaching the ideal Shockey-Queisser value), large absorption coefficient (>10<sup>5</sup> cm<sup>-1</sup>), decent

carrier mobility (~10 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) and long carrier lifetime (~60 ns).<sup>[9-11]</sup> Furthermore, Sb<sub>2</sub>Se<sub>3</sub> possesses advantages of low-toxicity, low-cost and earth-abundant constitutes, the only one stable crystalline phase can also get rid of complex composition and secondary phase control during thin film deposition process. According to theoretical calculations, the PCE of Sb<sub>2</sub>Se<sub>3</sub> can be as high as 30%, further strength its competitiveness as a new photovoltaic material.<sup>[12,13]</sup>

Great progress for Sb<sub>2</sub>Se<sub>3</sub> solar cells has been achieved in the last decade, obtaining the current efficiency record of 3.21% for Sb<sub>2</sub>Se<sub>3</sub> mesoporous sensitized-type,<sup>[14]</sup> 7.62% for planar heterojunction geometry-type<sup>[15]</sup> and the highest 9.2% for core-shell structured Sb<sub>2</sub>Se<sub>3</sub> nanorod array solar cells.<sup>[16]</sup> By comparison, planar heterojunction Sb<sub>2</sub>Se<sub>3</sub> solar cells are proven to have better performances than sensitized mesoporous solar cells because of the diversity of substrates, the tunability of interfaces and various deposition methods for the absorber layer. Sb<sub>2</sub>Se<sub>3</sub> absorbing films have been successfully prepared using various methods such as electrochemical deposition,<sup>[17]</sup> solution processing,<sup>[18]</sup> thermal (or rapid thermal) evaporation,<sup>[19,20]</sup> closed-space sublimation,<sup>[21]</sup> vapor transport deposition<sup>[10]</sup> and the magnetron sputtering.<sup>[22]</sup> Among these methods, magnetron sputtering can be considered as an effective deposition technique with distinct advantages like full-vacuum operation, accurate composition transfer from targets to films, good uniformity over large areas and competitive industrial scale-up. Our group has made great efforts to prepare Sb<sub>2</sub>Se<sub>3</sub> thin film solar cells via magnetron sputtering and recently achieved an interesting PCE of 6.06% as well as a highest V<sub>OC</sub> value of 494 mV.<sup>[22-24]</sup> Sb<sub>2</sub>Se<sub>3</sub> thin film prepared by magnetron

sputtering combined with post-selenization has benign growth orientation, accurate chemical composition and reduced deep level defect density. Despite these endeavors, as an important part, the studies on the sputtering target are rarely reported, especially the concern to construct a facile and versatile path for targets preparation. Compared with the commercial sputtering targets, the homemade targets could have many advantages, such as reducing the cost significantly, tailoring the chemical composition independently and realizing pristine doping efficiently, thus needs further investigation.

In this work, an effective method of ball milling followed with spark plasma sintering (SPS) was used to prepare high-quality Sb<sub>2</sub>Se<sub>3</sub> sputtering target. Then the Sb<sub>2</sub>Se<sub>3</sub> absorbing thin films have been prepared by using radio frequency (RF) magnetron sputtering with an additional post-selenization heat treatment. A champion Sb<sub>2</sub>Se<sub>3</sub> thin film solar cell with substrate configuration of Mo/Sb<sub>2</sub>Se<sub>3</sub>/CdS/ITO/Ag can achieve an interesting PCE of 5.08%. The combined features of homemade sputtering target and advantageous thin film preparation further demonstrated its attractive potential for thin film photovoltaic applications.

## 2. Experimental details

# 2.1. Preparation of Sb<sub>2</sub>Se<sub>3</sub> target

An effective method of ball milling combined with SPS process using 30 g of high purity Sb<sub>2</sub>Se<sub>3</sub> particles (99.99%, Advanced Material Professional Manufacture, 100 meshes) as raw materials was used to prepare Sb<sub>2</sub>Se<sub>3</sub> target. A schematic illustration of the preparation process is shown in Fig. 1. The ball milling was performed at room temperature in a vertical planetary ball mill using hardened steel balls and stainless steel cell, after 6 hours with a speed of 300 rpm/min, fine Sb<sub>2</sub>Se<sub>3</sub> powder can be obtained. The SPS process was carried out by using an apparatus Labox-325 SPS. The as-milled Sb<sub>2</sub>Se<sub>3</sub> powder was placed inside a graphite die of 60 mm diameter and covered with a thin carbon layer. A fixed pressure of 30 KN was applied before running the two-step heating procedures, specifically, increasing the temperature from room temperature to 300 °C with a heating rate of 20 °C/min firstly and then further increasing to 420 °C with a slower rate of 10 °C/min. After 5 min dwell, the electric current was turned off, the pressure was released and the sample was cooled down to room temperature. Finally, the bulk sample was taken out and the surface was finely polished to obtain a qualified homemade magnetron sputtering target with diameter of 60 mm and a thickness of approximately 2 mm. The target was closely bonded onto a copper backing plate using indium in order to improve its heat dissipation ability.

# 2.2 Preparation of Sb<sub>2</sub>Se<sub>3</sub> thin film solar cell

Sb<sub>2</sub>Se<sub>3</sub> thin films were prepared by using RF magnetron sputtering involved with post-selenization heat treatment, as depicted in Fig. 1. Based on the homemade Sb<sub>2</sub>Se<sub>3</sub> target, Mo-coated soda lime glass was chosen as device substrate. Prior to sputtering, it was ultrasonically cleaned in sequential detergent, acetone, isopropanol and ethanol solution for 10 min, respectively. The chamber was evacuated to a residual pressure of less than  $8.0 \times 10^{-4}$  Pa before each deposition. Argon gas was introduced at a rate of 40 sccm and the deposition was carried out with a fixed power of 35 W also with a relatively low pressure of 1.0 Pa. The deposition time was 90 min with an

approximate rate of 10 nm/min. After that, a post-selenization heat treatment was applied in order to eliminate the possible detrimental selenium vacancies and obtain crystalline Sb<sub>2</sub>Se<sub>3</sub> thin films. In detail, high purity Se particles (99.999%, particle size: 1-6 mm, Aladdin) and the as-deposited thin film were separately placed into a double-chamber vacuum tubular furnace. The furnace was evacuated by using a mechanical pump and high purity argon gas was then introduced to maintain working pressure of 5×10<sup>4</sup> Pa. Temperature of the Se side was fixed at 400 °C to provide sufficient Se partial pressure, selenization of the thin films was last for 20 min at temperatures of 380 °C, 400 °C, 420 °C and 440 °C, respectively. All those temperatures were ramped to the setting values at a rate of 20 °C/min.

After the preparation of Sb<sub>2</sub>Se<sub>3</sub> thin film, CdS buffer layer was then deposited via chemical bath deposition method, an additional heat treatment at 300 °C for 5 min in argon atmosphere was used to induce elemental inter-diffusion and optimize the band alignment. Indium tin oxide (ITO) window layer was subsequently deposited using direct current (DC) magnetron sputtering under a power of 60 W, a pressure of 0.4 Pa and a flow rate of 30 sccm for argon and oxygen gas, respectively. Finally, the device surface was scribed into small squares with identical area and then low-temperature (60 °C) solidified Ag colloids were painted onto the surface to form metallic contact. Sb<sub>2</sub>Se<sub>3</sub> solar cell with substrate structure of Mo/Sb<sub>2</sub>Se<sub>3</sub>/CdS/ITO/Ag was prepared and used for performance measurements under an active device area of 0.15 cm<sup>2</sup>.

#### 2.3 Characterizations

The crystal structure of Sb<sub>2</sub>Se<sub>3</sub> thin films were characterized by X-ray diffraction

(XRD, Ultima-IV) with  $CuK_{\alpha}$  radiation under 40 kV and 40 mA. Morphologies of the thin films were observed using a Zeiss SUPRA 55 thermal field emission scanning electron microscope (SEM). A SEM-coupled Energy Dispersive X-ray Spectroscope (EDS, BRUKER QUANTAX 200) was also used to analyze the chemical compositions and the elemental distribution. Transmission electron microscope (TEM) measurements were performed on a FEI Titan Cubed Themis G2 300 microscope, the sample was prepared by ablating the single thin film solar cell using focused ion beam (FIB, FEI Scios). A Shimadzu UV-3600 UV/Vis/NIR spectrophotometer equipped with monochromator was used for the optical reflectance and transmittance investigation and using pure soda-lime glass as the substrate. Current density-voltage (J-V) curves were measured by using a multi-meter (Keithley, 2400 Series) under AM 1.5G light illumination from a 3A solar simulator with intensity calibrated to 100 mW/cm<sup>2</sup> through a Si reference cell. The voltage was forwardly and backwardly scanned from -0.1 V to 0.6 V with a scan rate of 0.01 V/s. The external quantum efficiency (EQE) spectra were obtained using a Zolix SCS101 system with a monochromator and a Keithley 2400 source meter.

## 3. Results and Discussion

Fig. 2a shows the XRD patterns of the pristine commercial Sb<sub>2</sub>Se<sub>3</sub> powder, the powder after ball milling and the as-prepared target after SPS. It can be seen that all the diffraction peaks match well with the JCPDS standard card (No. 15-0861) of the orthorhombic phase of Sb<sub>2</sub>Se<sub>3</sub> without any detectable impurities. Compared with pristine Sb<sub>2</sub>Se<sub>3</sub> powder, the absence of localized broad peak ( $17^{\circ}-27^{\circ}$ ) of the

ball-milled powder indicates a slight improvement of crystallinity due to the elimination of some amorphous particles under low-energy treatment. Moreover, the ball milling induced crystal size decrease can also be observed. According to the Scherrer equation, Dp=0.94 $\lambda/\beta_{1/2}\cos\theta$ , where Dp is crystal size,  $\lambda$  is wavelength,  $\beta_{1/2}$ is the full-width at half-maximum (FWHM) and  $\theta$  is the peak position.<sup>[25]</sup> Two major peaks of (221) and (240) figure out crystal size of 3.17 nm and 3.36 nm for the pristine powder, respectively. Then the values decrease to 2.25 nm and 2.90 nm after ball milling. The obtained finer powder with higher crystallinity is really beneficial for preparing high-quality Sb<sub>2</sub>Se<sub>3</sub> target. The XRD pattern of the Sb<sub>2</sub>Se<sub>3</sub> target also presents a modified preferential crystallographic orientation from (240) to (221) after SPS, which is reasonable to occur under the coaction of the pulsed electric current and the applied pressure.<sup>[26]</sup> Importantly, the special heating mechanism of SPS makes this technology capable of sintering Sb<sub>2</sub>Se<sub>3</sub> target at a lower temperature (420 °C), a faster heating rate (20 °C/min) and a shorter sintering time (5 min) than those of the conventional sintering technologies. Furthermore, the obtained target has a rather ideal relative density as high as 98% measured by using Archimedes drainage method.<sup>[27]</sup> As shown in Fig. 2b, the polished Sb<sub>2</sub>Se<sub>3</sub> target has flat and smooth surface without obvious cracks or holes. The representative cross-sectional SEM images of the target further confirm its highly dense and compact nature with a thickness approaching to 2 mm. Overall, the as-prepared target by ball milling and SPS meets the criteria for subsequent magnetron sputtering.

Fig. 3a presents the XRD patterns of the as-deposited and post-selenized Sb<sub>2</sub>Se<sub>3</sub>

thin films at different temperatures. For the as-deposited thin film, no diffraction peaks correspond to the crystalline phase can be observed except a single peak  $(2\theta=41^{\circ})$  belonging to Mo substrate, suggesting its amorphous nature. Afterwards, the thin film was annealed under selenium atmosphere (post-selenization) at four different temperatures of 380 °C, 400 °C, 420 °C and 440 °C, respectively. The XRD patterns of these post-selenized thin films exhibit prominent peaks in good agreement with the JCPDS standard card (No. 15-0861) of the orthorhombic phase of Sb<sub>2</sub>Se<sub>3</sub>. A slight increase of peak intensities with increasing the post-selenization temperature to 420 °C suggests the crystallinity improvement of the Sb<sub>2</sub>Se<sub>3</sub> thin films upon annealing. Moreover, three major diffraction peaks of (211), (221) and (301) show sharp characteristics, indicating the highly crystalline nature, also with a preferential growth orientation of (hk1). Plenty of studies have pointed out that such perpendicular growth of the Sb<sub>2</sub>Se<sub>3</sub> grains would reduce the recombination loss at grain boundaries, promote the carrier transport throughout absorber layer, thus improving the device performance.<sup>[15,20,28]</sup> However, once an excessively high selenization temperature (440 °C) was applied, the diffraction peak intensities of the Sb<sub>2</sub>Se<sub>3</sub> thin film with observable decrease was possibly due to its decomposition.

Fig. 3b-f presents the top-view SEM images of the as-prepared thin films. As shown in Fig. 3b, no obvious crystal grains can be observed for the as-deposited amorphous thin film. Fine particles were formed on the substrate due to the limited mobility of Sb<sub>2</sub>Se<sub>3</sub> molecules and weak surface diffusion during the sputtering process. The highly compact nature was also closely related to its low deposition pressure (1.0 Pa) according to the Thornton magnetron sputtering regional structure model at substrate temperature and Sb<sub>2</sub>Se<sub>3</sub> melting temperature ratio Ts/Tm of 0.34.<sup>[29]</sup> After post-selenized at 380 °C, the molecules were diffused under thermal motion and rearranged to form micron-sized Sb<sub>2</sub>Se<sub>3</sub> crystal grains. The existence of some pinholes on the surface can be attributed to the insufficient crystallization and growth process (Fig. 3c), consistent with the XRD result. Further increasing the post-selenization temperature to 400 °C and 420 °C, it leads to a more dense and uniform crystalline thin film accompanied by columnar growth of ellipsoid grains with an average size of approximately 750 nm, which is advantageous for suppress the recombination loss at the grain boundaries. However, if the temperature is too high, e.g., 440 °C, as depicted in Fig. 3f, though some crystal grains become larger, thermal induced the formation of distinct micro-voids due to Se evaporated from the as-deposited Sb<sub>2</sub>Se<sub>3</sub> thin film under its high vapor pressure nature, which could produce shunt paths and cause severe current leakage. Therefore, it is crucial to control the post-selenization temperature to obtain high-quality Sb<sub>2</sub>Se<sub>3</sub> absorber layer with high crystallinity and benign growth orientation.

The elemental composition of the as-prepared target, as-deposited thin film and the post-selenized thin films were obtained from SEM-coupled EDS analysis. As shown in Table 1, the Sb<sub>2</sub>Se<sub>3</sub> target has a slight Se poor with Sb/Se ratio of 0.72 and it possibly occurred due to the applied energy and/or heat during ball-milling and SPS processes. The as-deposited amorphous thin film has a quite similar composition with the target, confirming an accurate composition transfer character for this

advantageous RF magnetron sputtering. An additional post-selenization heat treatment was designed to induce crystallization and also compensate the pristine Se loss. As expected, the post-selenized crystalline thin films show an overall increased Se content, an optimal ratio of 0.66 obtained at 420 °C is close to the standard stoichiometric ratio of 0.67 for Sb<sub>2</sub>Se<sub>3</sub>. Moreover, the decreased Se content at 440 °C is also consistent with the SEM observations under the existence of Se-deficit micro-voids.

To investigate the optical properties of the as-prepared Sb<sub>2</sub>Se<sub>3</sub> thin films, UV/Vis/NIR spectrophotometer has been performed to obtain the reflection and transmission spectra of the thin films using glass as substrate and covering a range from 300 nm to 1500 nm. As shown in Fig. 4a and Fig. 4b, a prominent difference of reflectance and transmittance between the amorphous thin film and crystalline Sb<sub>2</sub>Se<sub>3</sub> thin films can be observed, which can be assigned to an intrinsic evolution of the atomic arrangement changed from disorder to order. The obvious red-shift of the absorption region observed in reflection spectra, accompanied by the synchronous red-shift of the short wavelength cut-off edge from 700 nm for the amorphous thin film to about 860 nm for the crystalline thin film, both clearly imply the variation of band gap. To specify the real value, it can be calculated according to the following formulas:

$$\alpha = \frac{1}{d} \ln \left( \frac{1 - R(\lambda)}{T(\lambda)} \right) \tag{1}$$

$$\alpha hv = C(hv - E_g)^n \tag{2}$$

where  $\alpha$  is the absorption coefficient, d is the thickness, R and T are the reflectance

and transmittance, respectively.<sup>[30]</sup> The latter is a typical Tauc formula, where C is a constant, h is the Planck's constant, v is the photon frequency, n is an index defined by 0.5 for direct and 2.0 for indirect bandgap semiconductor.<sup>[31]</sup> The as-deposited amorphous thin film has a direct band gap of 1.68 eV, then the post-selenization induced the value decrease to 1.33 eV, 1.29 eV, 1.27 eV and 1.19 eV for the Sb<sub>2</sub>Se<sub>3</sub> thin films underwent 380 °C, 400 °C, 420 °C and 440 °C heat treatment, respectively. Notably, the calculated band gap agree well with that given in prior publications for crystalline Sb<sub>2</sub>Se<sub>3</sub> thin films.<sup>[23]</sup> Moreover, the optimal Sb<sub>2</sub>Se<sub>3</sub> thin film post-selenized at 420 °C with a band gap of 1.27 eV can be considered as an efficient absorber layer in thin film photovoltaic applications.

Compared with the widely investigated superstrate Sb<sub>2</sub>Se<sub>3</sub> thin film solar cells, the solar cells with substrate configuration have many advantages, such as tailoring the absorber layer independently, engineering the interface efficiently and fabricating flexible or tandem solar cells facile.<sup>[32]</sup> Herein, Sb<sub>2</sub>Se<sub>3</sub> thin film solar cell with substrate structure of Mo/Sb<sub>2</sub>Se<sub>3</sub>/CdS/ITO/Ag was prepared and a schematic illustration of this device is shown in Fig. 5a. The representative cross-sectional SEM image of the device (Fig. 5b) displays obvious layered structure with approximate thickness of 850 nm, 60 nm and 500 nm for Sb<sub>2</sub>Se<sub>3</sub>, CdS and ITO layer, respectively. The Sb<sub>2</sub>Se<sub>3</sub> absorber layer is consisted of large crystal grains with columnar growth. The interface between Sb<sub>2</sub>Se<sub>3</sub> and CdS also shows compact, well-adherent and pinhole-free characteristics, which is beneficial for reducing charge carrier recombination and current leakage. Furthermore, the corresponding EDS elemental

mappings marked with Mo, Sb, Se, Cd, S and In are also conducted to confirm the compositional distribution. Elements of Sb and Se present good uniformity throughout the whole Sb<sub>2</sub>Se<sub>3</sub> absorber layer, confirming the high quality of this post-selenized Sb<sub>2</sub>Se<sub>3</sub> thin film. Notably, an observable Cd inter-diffusion is reasonable to occur because of the additional post-annealing of the device, which has been reported to be beneficial for obtaining favorable band alignment and reducing the recombination at the heterojunction interfaces.<sup>[33]</sup>

Fig. 6 shows the champion device performances based on the Sb<sub>2</sub>Se<sub>3</sub> thin film post-selenized at 420 °C. According to the current density-voltage (J-V) curve (Fig. 6a), under the simulated AM1.5G solar irradiation, the device offers a short-circuit current density (J<sub>SC</sub>) of 23.0 mA/cm<sup>2</sup>, an open circuit voltage (V<sub>OC</sub>) of 480 mV, and a fill factor (FF) of 46.0%, thus achieving a power conversion efficiency of 5.08%. In addition, no obvious hysteresis between the forward ( $J_{SC}$  to  $V_{OC}$ ) and backward ( $V_{OC}$ to J<sub>SC</sub>) scans can be observed in our device, suggesting the high-quality Sb<sub>2</sub>Se<sub>3</sub> absorber layer and the reasonable substrate device configuration.<sup>[34]</sup> Importantly, the obtained device performances are comparable to that of state-of-the-art Sb<sub>2</sub>Se<sub>3</sub> thin film solar cells.<sup>[11,24,35]</sup> As shown in Fig. 6b, the external quantum efficiency (EQE) spectrum reveals the photo-response covering a broad UV-visible-NIR range, which agrees well with the narrow band gap of Sb<sub>2</sub>Se<sub>3</sub>. The maximum value can reach higher than 80%, implying less recombination losses at the well-adherent Sb<sub>2</sub>Se<sub>3</sub>/CdS interface as well as in the bulk absorber layer. Wherein, the as-prepared Sb<sub>2</sub>Se<sub>3</sub> thin film with high crystallinity and advantageous preferential orientation can effectively

induce bulk defects passivation. Finally, the integrated  $J_{SC}$  calculated from EQE data is also drawn in Fig. 6b, a value of 20.8 mA/cm<sup>2</sup> is comparable to the J-V measurement result.

To further confirm the high quality of Sb<sub>2</sub>Se<sub>3</sub>/CdS interface as well as the Sb<sub>2</sub>Se<sub>3</sub> absorber layer, morphological and structural characterizations of the champion device by TEM are shown in Fig. 7. The existence of layered structure with specific thickness is consistent with SEM results (Fig. 7a). High-resolution TEM (HRTEM) analysis was performed at the Sb<sub>2</sub>Se<sub>3</sub>/CdS interface, though it is not exactly epitaxial growth of CdS on the Sb<sub>2</sub>Se<sub>3</sub> layer due to their lattice mismatch, a smooth and adherent interface can be observed, corresponding to the elemental inter-diffusion. The absence of crystal lattice distortion or amorphous layer at the interface region further demonstrates its efficient generation and separation of photo-carriers. Afterwards, HRTEM images correspond to three arbitrary points 1, 2 and 3 that were randomly selected near the top, middle and bottom regions of the Sb<sub>2</sub>Se<sub>3</sub> absorber layer were measured, as shown in Fig. 7c-e. All the three points show quite similar lattice fringes with interplanar d-spacings of approximately 0.289 nm and 0.316 nm that agree well with the distance of the (221) and (211) lattice planes of the orthorhombic phase Sb<sub>2</sub>Se<sub>3</sub>. This preferential growth is consistent with its pristine target and closely related to a proper post-selenization treatment. According to the recent theoretical and experimental studies, it is indeed determined intrinsically by the anisotropic Sb-Se atom chain and layer structure of Sb<sub>2</sub>Se<sub>3</sub>.<sup>[36,37]</sup> Furthermore, such a vertical crystal growth orientation across the whole Sb<sub>2</sub>Se<sub>3</sub> thin film will greatly facilitate charge carrier transport within the absorber layer and thus improving the final device performance.

#### 4. Conclusions

In summary, a facile method of ball milling combined with SPS process has been successfully developed to prepare compact and dense Sb<sub>2</sub>Se<sub>3</sub> target with smooth surface. Sb<sub>2</sub>Se<sub>3</sub> thin films can be prepared by RF magnetron sputtering using the homemade target also with an additional post-selenization heat treatment at different temperatures. The as-deposited thin film shows amorphous nature and then the highly crystalline thin film consisted of large crystal grains can be obtained after post-selenization treatment. A systematic investigation of temperature-induced crystallization, preferential orientation, stoichiometric ratio variation, surface morphologies evolution and optical properties modification conclude an optimal post-selenization temperature of 420 °C. Efficient Sb<sub>2</sub>Se<sub>3</sub> thin film solar cell with substrate structure of Mo/Sb<sub>2</sub>Se<sub>3</sub>/CdS/ITO/Ag was fabricated. The champion device with highly interesting PCE of 5.08% ( $J_{SC}=23.0 \text{ mA/cm}^2$ ,  $V_{OC}=480 \text{ mV}$ , FF=46.0%) and maximum EQE value higher than 80% has been achieved. Further morphological and structural characterizations confirm the positive effects of proper preferential orientation of the Sb<sub>2</sub>Se<sub>3</sub> absorber layer and smooth contact of the Sb<sub>2</sub>Se<sub>3</sub>/CdS heterojunction interface on such superior device performances.

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**Fig. 1.** Schematic illustration of the preparation process of the substrate structured Sb<sub>2</sub>Se<sub>3</sub> thin film solar cells. (a) Sb<sub>2</sub>Se<sub>3</sub> fine powder obtained by ball milling, (b) Sb<sub>2</sub>Se<sub>3</sub> target obtained by SPS process, (c) Sb<sub>2</sub>Se<sub>3</sub> thin film deposition by RF magnetron sputtering, (d) Post-selenization heat treatment, (e) CdS buffer layer deposition via CBD method, (f) Representative photographs of the device, surface morphologies of device after ITO layer deposited and Ag electrodes painted.



**Fig. 2.** (a) XRD patterns of the pristine commercial Sb<sub>2</sub>Se<sub>3</sub> powder, the powder after ball milling and the as-prepared target after SPS, (b) Surface morphology and (c) Cross-sectional SEM images of the Sb<sub>2</sub>Se<sub>3</sub> target.



Fig. 3. Characterizations of the Sb<sub>2</sub>Se<sub>3</sub> thin films post-selenized at different temperatures: (a) XRD patterns, (b-f) Top-view SEM images of the thin films post-selenized at temperatures of (b) as-deposited, (c) 380 °C, (d) 400 °C, (e) 420 °C and (f) 440 °C.

 Table 1. Elemental composition of the Sb<sub>2</sub>Se<sub>3</sub> target and Sb<sub>2</sub>Se<sub>3</sub> thin films obtained

 from EDS analysis

Element	Target	As-deposited	380 °C	400 °C	420 °C	440 °C
Sb (at%)	41.9	41.77	40.80	38.77	39.91	42.58
Se (at%)	58.1	58.23	59.20	61.23	60.09	57.42
Sb/Se	0.72	0.72	0.69	0.63	0.66	0.74



Fig. 4. Optical characterizations of the Sb<sub>2</sub>Se<sub>3</sub> thin films as a function of wavelength and with different post-selenization temperatures. (a) Reflection spectra, (b) Transmission spectra and (c) Plot of  $(\alpha hv)^2$  versus hv, used to obtain direct band gap.



**Fig. 5.** (a) Schematic configuration of the  $Sb_2Se_3$  thin film solar cell. (b) Cross-sectional SEM image of the device and (c) the corresponding EDS elemental mappings of Mo, Sb, Se, Cd, S and In, used to reveal the compositional distribution.



**Fig. 6.** J-V curves of the champion  $Sb_2Se_3$  thin film solar cell under forward scan and backward scan. (b) EQE and integrated  $J_{sc}$  of the device.



**Fig. 7.** Morphological and structural characterizations of the champion Sb<sub>2</sub>Se<sub>3</sub> thin film solar cell. (a) Cross-sectional TEM image of the device, (b) HRTEM image of the Sb<sub>2</sub>Se<sub>3</sub>/CdS interface, (c-e) Lattice fringes correspond to three arbitrary spots 1, 2 and 3 across the Sb<sub>2</sub>Se<sub>3</sub> absorber layer selected in (a) and performed by HRTEM.