



Grain engineering of solution-processed Sb₂S₃ thin film by tuning precursor fabrication environments

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ABSTRACT

Antimony sulfide (Sb₂S₃) has garnered significant attention recently due to its remarkable photovoltaic properties and low toxicity. However, the conventional physical vapor deposition approach faces challenges in achieving high-quality films due to Sb₂S₃ having a quasi-one-dimensional nanoribbon structure. In contrast, solution-processed Sb₂S₃ thin films have shown improved photovoltaic behavior, offering a low-cost and scalable fabrication method. Nonetheless, the sensitivity of the solution process to the chemical composition of the precursor poses a challenge, often requiring noble gas protection to prevent exposure to toxic solvents or moisture-sensitive chemicals. Despite this, the impact of precursor fabrication conditions on film growth behavior remains unexplored. In our study, we investigate how different processing atmospheres of precursors, namely nitrogen (N₂) and air, affect grain growth and the associated optical and electronic performance of Sb₂S₃ thin films. Our findings reveal that the presence of oxygen in the precursor can hinder grain growth by obstructing surface integration sites, resulting in undesired (hk0) orientation and even the formation of Sb₂O₃ on the surface of the Sb₂S₃ films, despite identical post-deposition conditions. This research sheds light on how the ambient conditions during precursor preparation can influence grain engineering, thereby providing valuable insights for controlling the grain size and producing high-quality Sb₂S₃ absorber films.

1. Introduction

Antimony sulfide, i.e., Sb₂S₃ thin film solar cell has garnered considerable attention, primarily due to its optimal bandgap (approximately 1.7 eV), high absorption coefficient (approximately $1.8 \times 10^5 \text{ cm}^{-1}$), earth abundance, and environmentally friendly characteristics (Myagmarsereejid et al., 2021; Ning et al., 2021; Zheng et al., 2019; Cao et al., 2022a; Tao et al., 2019). Sb₂S₃ has a quasi-one-dimensional structure with the unit of (Sb₄S₆)_n ribbons, determining photo-generated carriers transport rapidly along the (hk1) direction (Jin et al., 2020; Cao et al., 2022b; Pan et al., 2023). To date, several growth methods have been investigated to synthesize high-quality Sb₂S₃ absorbers, including close space sublimation (Guo et al., 2019), spin coating (Kaenbourg et al., 2018a), and hydrothermal method (Zhou et al., 2022). Especially, the physical vapor deposition of the Sb₂S₃ possesses relatively lower performance for the solar cell device performance due to the challenges of controlling the grain orientation at a fast growth speed (Guo et al., 2019; Zhang et al., 2020; Du et al., 2022). Chemical solution approach stands out for its convenience,

cost-effectiveness, and ease of upscale manufacturing.

Grain boundaries play a crucial role in governing the optoelectronic properties of polycrystalline optoelectronic materials (Fukuda et al., 2023; Hao et al., 2023). The presence of dangling bonds at grain boundaries can trap carriers, acting as nonradiative recombination centers. Therefore, it becomes imperative to increase grain size, as grain boundary densities can be minimized. However, grain growth behavior is difficult to control in Sb₂S₃ absorbers (Liu et al., 2024). So far, it is reported that the introduction of the Ce ions in the Sb₂S₃ precursors could significantly impact the grain growth and regulate the grain size of the Sb₂S₃, impacting the device performance (Liu et al., 2024). The nucleation and crystal growth of the film heavily depend on the in-situ chemical conditions of precursors for film deposition. For example, oxygen in the precursor plays a key role in regulating the crystallization process of materials, such as Nb₃Sn (Sun et al., 2023) and graphene (Chuang and Woon, 2016). Most of the solution-processed Sb₂S₃ films still need noble gas protection during the thin film growth, e.g., N₂ gas-filled glovebox. How residual oxygen gas in the Sb₂S₃ precursor impacts the grain growth behavior is unclear.

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In this study, we investigate how the residual oxygen gas in the precursor impacts the Sb_2S_3 grain growth and grain size. It is obtained that the introduction of oxygen in the precursors results in a smaller Sb_2S_3 film grain size, undesired ($hk0$) grain orientation, and formation of Sb_2O_3 on the surface. It indicates that oxygen molecules dissolved in the Sb_2S_3 precursor could impede crystal growth by blocking surface integration sites, leading to a smaller grain size. These residual oxygen molecules also assist the formation of pinholes. This study provides valuable insights into the importance of controlling the precursor processing conditions for achieving large grain and pinhole-free Sb_2S_3 , which is crucial for enhancing the performance of corresponding solar cells.

2. Experimental

2.1. Materials

Sb_2O_3 (Alfa Aesar, 99.999%), Ethanol (Alfa Aesar, 94%–96%), Carbon disulfide (Alfa Aesar, 99.9%), and n-butylamine (Alfa Aesar, 98%) were purchased from Alfa Aesar and used without further purification.

2.2. Preparation of Sb_2S_3 precursor solutions

The precursors were prepared following the procedure previously reported, under ambient air and N_2 conditions, respectively (Wang et al., 2017). Sb_2O_3 , utilized as the antimony source, was dispersed within a

solution containing diluted carbon disulfide (CS_2) in ethanol. Subsequently, n-butylamine was added dropwise to the mixed solution. Before use, the precursor was stirred in air and N_2 , and indexed as Sb_2S_3 -air and Sb_2S_3 - N_2 , respectively. To enhance the dissolution of oxygen in the solution, the precursor, prepared in the open air, was aerated by bubbling air during stirring. Solutions from both processing environments appeared clear and were fully dissolved, which rules out the possibility that the Sb_2O_3 detected by XPS originates from the starting chemical. Note that both films from precursors prepared in air and N_2 were annealed in the dry N_2 -supplied glovebox to investigate the influence of precursor processing conditions.

2.3. Solar cell fabrication and characterization

Fabrication: F-doped SnO_2 -coated soda-lime glass (FTO) substrates were sequentially cleaned with detergent, acetone, isopropyl alcohol, and deionized water in an ultrasonic bath, with each step lasting 10 min. CdS window layers (~ 100 nm) were then deposited on the cleaned FTO using the chemical bath deposition (CBD) method previously reported (Guo et al., 2018). The Sb_2S_3 precursor, prepared in the air, was subsequently transferred to the dry N_2 -filled glovebox. Both precursors, prepared in air and N_2 were spin-coated onto the CdS-coated FTO substrate at 6000 rpm for 30 s, followed by pre-annealing at 200°C for 2 min and final annealing at 340°C for 2 min in the glovebox (O_2 and $\text{H}_2\text{O} < 0.1$ ppm). The best crystallization conditions were optimized through 30 trials. The carbon electrodes were blade-coated with carbon paste (with

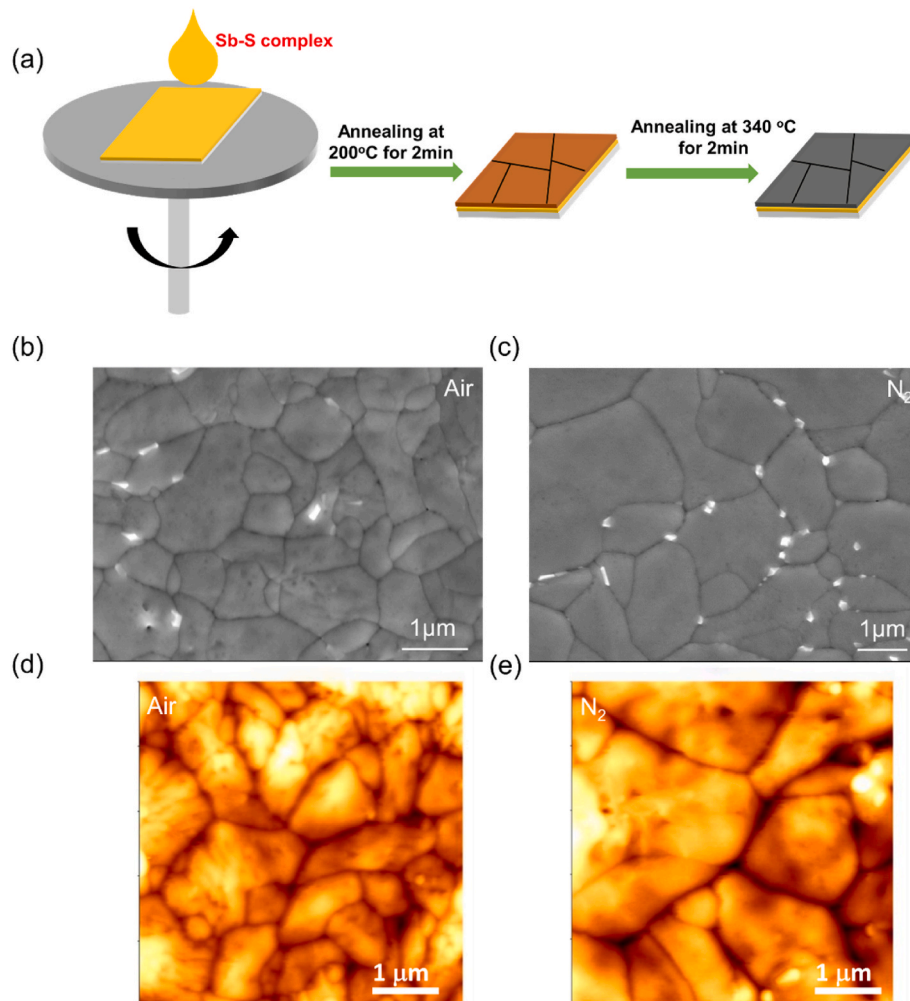


Fig. 1. Sb_2S_3 films deposition process and surface morphology of Sb_2S_3 films. (a) Schematic depictions of Sb_2S_3 films deposition process. Scanning electron microscopy (SEM) of (b), Sb_2S_3 -air and (c), Sb_2S_3 - N_2 films. Atomic force microscopy (AFM) of (d), Sb_2S_3 -air and (e), Sb_2S_3 - N_2 films.

an active area of 0.08 cm^2) to form the solar cells. The highest device efficiencies in each case were identified over the course of the optimization of 20 devices. Throughout the following paragraphs, we will refer to these films as Sb_2S_3 -air and Sb_2S_3 - N_2 films, respectively.

Characterization: The structural characterization of the films was performed by X-ray diffraction (Philips X'Pert MPD) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5416 \text{ \AA}$) at a tube voltage of 45 kV and current of 40 mA. A scan speed of $6.79^\circ/\text{min}$ was employed to collect the XRD data (2θ range = 10 – 70°). The X-Ray instrument is equipped with a goniometer for angular movement.

Film morphology was determined using scanning electron microscope (SEM, JEOL 7000 FE) and atomic force microscopy (AFM, Park XE70). SEM images were obtained using the JEOL 7000 FE-SEM (Tokyo, Japan) at $15\,000\times$ magnification, with a working distance of 10.0 mm and an accelerating voltage of 10.0 kV in the SE imaging mode. The AFM topography was obtained in contact mode through a Pt/Ir coated contact probe (ANSCM-PT from AppNano, Inc.). The cantilever spring constant was around 3N/m, and resonance frequency was $\sim 60 \text{ kHz}$. AFM images were collected in FMM head mode with a scan rate of 1 Hz.

The chemical oxidation states of the Sb_2S_3 films were analyzed using X-ray photoelectron spectroscopy (XPS) on the Kratos Axis DLD spectrometer equipped with a monochromatic Al $\text{K}\alpha$ source ($h\nu = 1486.6 \text{ eV}$) under a vacuum of 10^{-10} Torr. The sample charging issues were calibrated using the standard carbon peak C 1s (284.8 eV) as a reference. Peak fitting and deconvolution were conducted by CasaXPS software, using Lorentzian Asymmetric lineshape and Shirley background subtraction. Survey spectra were acquired in the BE range of 1200–0 eV at room temperature, with an analyzer pass energy of 160 eV and an energy step size of 1 eV. High-resolution spectra were obtained with a pass energy of 20 eV and a step size of 0.1 eV.

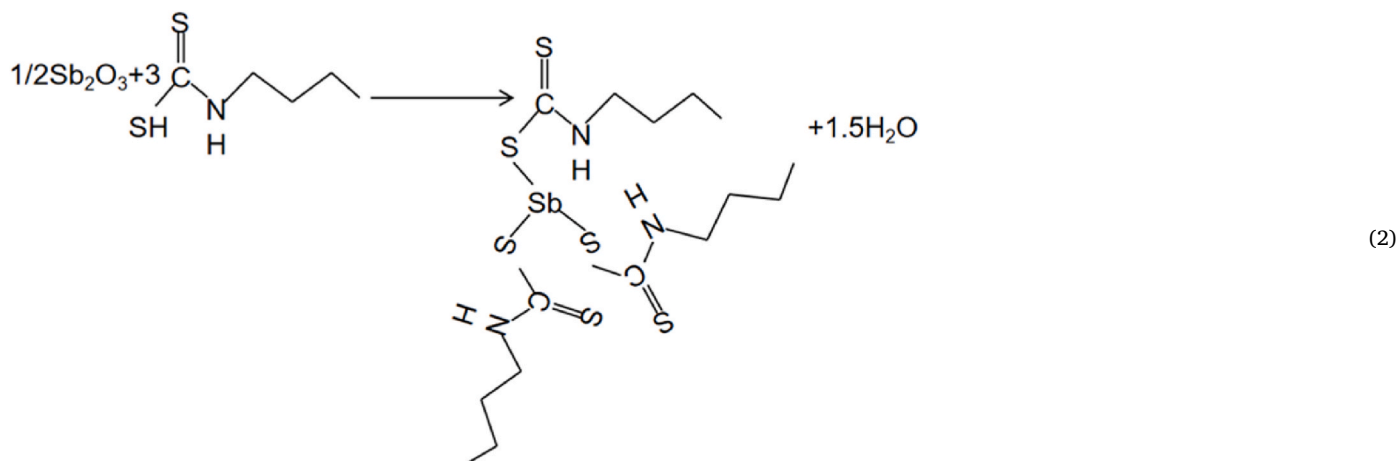
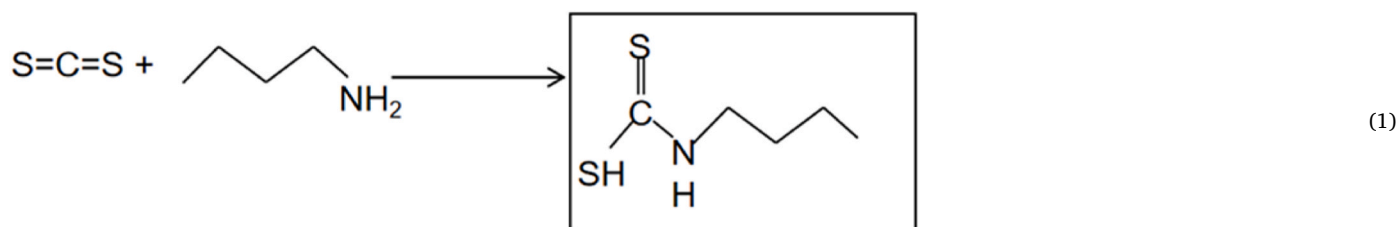
The absorber layer's light absorbance and transmittance spectra were measured using a UV-Vis spectrometer (Shimadzu UV-1800) over a wavelength range from 300 nm to 1100 nm, with a step size of 10 nm.

Current density-voltage (J-V) characteristics were measured by the Newport Sol3A class AAA solar simulator (Oriel, model 94023 A; Newport Corporation, Irvine, CA, USA) under ambient conditions (room temperature, 1000 W/m, air mass 1.5-G illumination). A Keithley 2420 source meter (Keithley Instrument Inc.) was used to acquire J-V characteristics. A calibrated Si-reference cell and meter (Newport, 91150 V, certified by NREL) were used to calibrate the solar simulator prior to the measurement. The voltage was swept from -0.2 V to 1.2 V with 101 sweep points and a dwell time of 10 ms.

External quantum efficiency (EQE) of solar cells was measured using a solar cell spectral response measurement system (QE-T, Enli Technology, Co. Ltd). Measurements were taken over a wavelength range from 300 nm to 1100 nm with a step size of 10 nm. The data collection involved 8000 sampling points at a sample rate of 15.

3. Results and discussion

The deposition process of Sb_2S_3 films is illustrated schematically in Fig. 1a. Both the precursors prepared in N_2 and air (as detailed in the materials and methods section) were transferred into the N_2 -filled glovebox and spin-coated on the substrate. The films were then annealed at 200°C for solvent drying, followed by high-temperature annealing at 340°C for 2 min to promote crystal growth. Fig. 1b–c displays the surface morphology of Sb_2S_3 -air and Sb_2S_3 - N_2 films, as analyzed by scanning electron microscopy (SEM). It is shown that the Sb_2S_3 -air film showed a grain size of $\sim 1 \mu\text{m}$ while Sb_2S_3 - N_2 film has a much larger grain size (~ 2 or $3 \mu\text{m}$). The AFM images (Fig. 1d–e) also indicate a larger grain size for the Sb_2S_3 - N_2 film, with a root mean square (RMS) roughness of $\sim 16.23 \text{ nm}$, whereas the Sb_2S_3 -air film exhibits an RMS roughness $\sim 19.82 \text{ nm}$. The grain orientation of Sb_2O_3 differs from that of Sb_2S_3 , which could be a contributing factor to the high surface roughness observed in the Sb_2S_3 -air film. The potential chemical reactions involved in the formation of Sb_2S_3 are listed below:



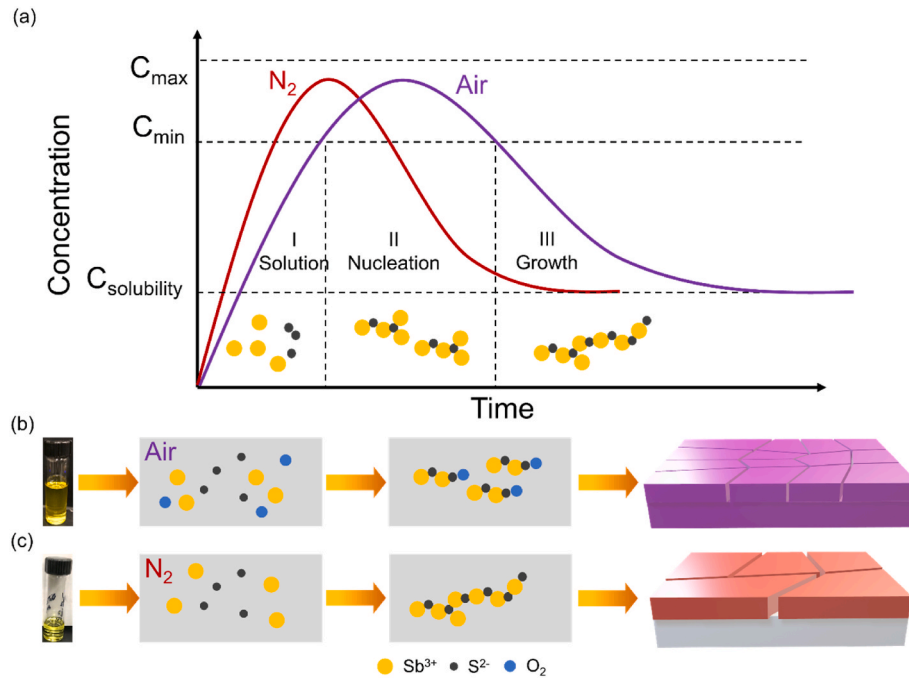


Fig. 2. Crystal growth of Sb_2S_3 -Air and Sb_2S_3 - N_2 films. (a) LaMer diagram illustrates the generation of atoms, nuclei, and the subsequent growth of the nuclei. Schematic illustrations depict the growth of (b), Sb_2S_3 -Air thin film and (c), Sb_2S_3 - N_2 thin film.

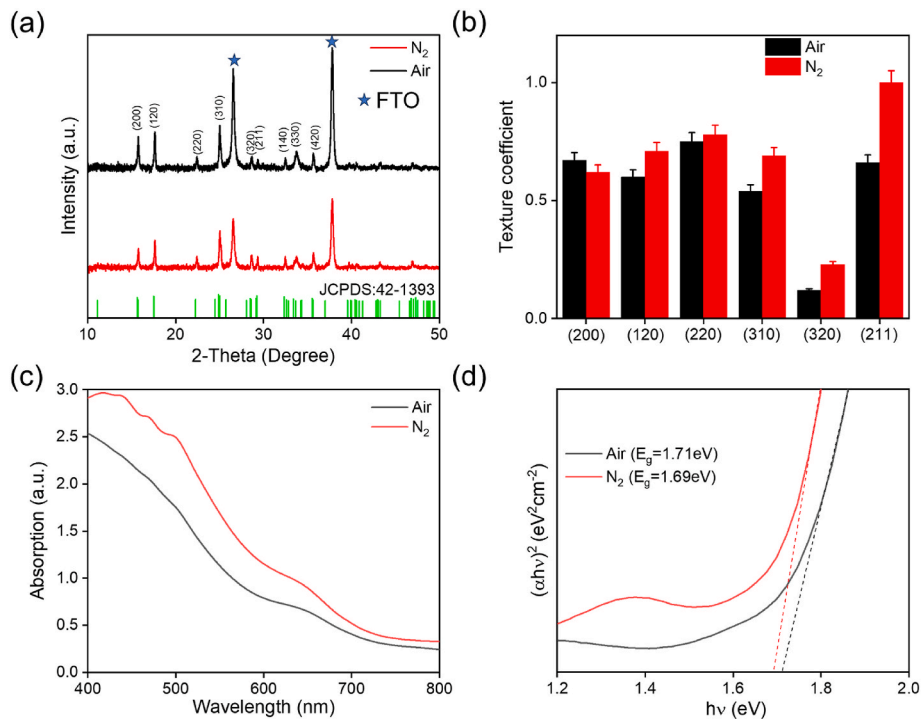


Fig. 3. Grain orientation and bandgap of Sb_2S_3 - N_2 and Sb_2S_3 -air films. (a), X-ray diffraction (XRD) patterns of Sb_2S_3 - N_2 and Sb_2S_3 -air films. (b), Texture coefficient of Sb_2S_3 films calculated from XRD results. The error bar represents 95% confidence limit. (c), Absorption spectra and (d), Tauc plot of Sb_2S_3 -air and Sb_2S_3 - N_2 films.

The Sb complex will decompose into Sb_2S_3 at high temperatures. The nucleation and crystal growth can be described by the LaMer model, as exhibited in Fig. 2a. After the spin-coating process, during low-temperature annealing, the concentration of precursors increases, approaching supersaturation concentration where nucleation begins (Stage I). Nuclei grow with the diffusion of precursor solutes (Stage II). When the solute is consumed faster than the evaporation of the

precursor solvent, the concentration falls below supersaturation concentration, leading to the exclusive growth of nuclei without the formation of new nuclei (Stage III) (Abbas et al., 2020). The oxygen molecules in the Sb_2S_3 -Air precursor serve as impurities, suppressing crystal growth by blocking integration sites (Derdour et al., 2011). Detailed crystal growth mechanisms are shown in Fig. 2b and c. In the presence of oxygen in the precursor, the diffusion rate of the solute may

Table 1Texture coefficient of $\text{Sb}_2\text{S}_3\text{-N}_2$ and $\text{Sb}_2\text{S}_3\text{-air}$ films with normalization.

	(200)	(120)	(220)	(310)	(320)	(211)
$\text{Sb}_2\text{S}_3\text{-N}_2$ film	0.62	0.71	0.78	0.69	0.23	1
$\text{Sb}_2\text{S}_3\text{-N}_2$ film error bar ($\pm$)	0.03	0.04	0.04	0.04	0.01	0.05
$\text{Sb}_2\text{S}_3\text{-Air}$ film	0.67	0.60	0.75	0.54	0.12	0.66
$\text{Sb}_2\text{S}_3\text{-Air}$ film error bar ($\pm$)	0.03	0.03	0.04	0.03	0.01	0.03

slow down, leading to predominance of the nucleation process. Conversely, when the precursor lacks oxygen, slow solvent evaporation occurs along with a rapid diffusion rate of the solute, leading to a larger grain size in $\text{Sb}_2\text{S}_3\text{-N}_2$ (Abbas et al., 2020). In addition, the $\text{Sb}_2\text{S}_3\text{-N}_2$ film displayed fewer pinholes than that of the $\text{Sb}_2\text{S}_3\text{-Air}$ film as shown in Fig. 1b and c. The formation of pinholes in the $\text{Sb}_2\text{S}_3\text{-Air}$ film is attributed to the introduction of oxygen during precursor preparation, which may trigger a degassing process during film growth, leading to the formation of pinholes (Hao et al., 2020). However, fewer pinholes still exist in the $\text{Sb}_2\text{S}_3\text{-N}_2$ film. That is possibly due to rapid annealing, lasting only for 2 min, resulting in incomplete crystallization of the film. Moreover, lots of white particles observed along the grain boundaries observed in both films are likely residual nuclei of Sb_2S_3 resulting from the crystal growth process (Wang et al., 2017).

Fig. 3a presents the X-ray diffraction (XRD) patterns of $\text{Sb}_2\text{S}_3\text{-Air}$ and $\text{Sb}_2\text{S}_3\text{-N}_2$ films deposited on FTO/CdS substrates. Both $\text{Sb}_2\text{S}_3\text{-Air}$ and $\text{Sb}_2\text{S}_3\text{-N}_2$ films show the presence of the Sb_2S_3 phase without a secondary phase. The calculated texture coefficient based on the XRD results is exhibited in Fig. 3b, where the $\text{Sb}_2\text{S}_3\text{-N}_2$ film exhibits stronger intensity in $(hk1)$ peaks, such as (211), indicating that the $(\text{Sb}_4\text{S}_6)_n$ ribbons tend to grow normal to the substrate, while the $\text{Sb}_2\text{S}_3\text{-Air}$ film shows less intensity in $(hk1)$ orientation. The detailed texture coefficient for the films are shown in Table 1. The various growth behavior observed in Sb_2S_3 films may originate from the presence of oxygen incorporated into the precursor solution, which can impact the growth process. The optical absorption of Sb_2S_3 films was characterized using UV-Vis

spectroscopy as shown in Fig. 3c. $\text{Sb}_2\text{S}_3\text{-N}_2$ film demonstrates better light absorption across all wavelengths, potentially due to its dense, pinhole-free morphology and large grain size compared to $\text{Sb}_2\text{S}_3\text{-air}$ film, as shown in Fig. 1. Due to the phenomenon of grain boundary scattering (Kimmer et al., 2007; Henriquez et al., 2013), photons are more likely to be scattered in films with small grain sizes ($\text{Sb}_2\text{S}_3\text{-air}$ film) compared to those with larger grain sizes ($\text{Sb}_2\text{S}_3\text{-N}_2$ film). Consequently, less light would be absorbed by the $\text{Sb}_2\text{S}_3\text{-air}$ film. The bandgap of $\text{Sb}_2\text{S}_3\text{-air}$ and $\text{Sb}_2\text{S}_3\text{-N}_2$ films are determined as 1.71 eV and 1.69 eV, respectively, using Tauc fitting (Fig. 3d). These values are in good agreement with the reported results (Cai et al., 2020). The incorporation of oxygen in the precursor solution results in the formation of oxygen associated defects in the resulting Sb_2S_3 film (Cai et al., 2020; Lian et al., 2021; Kondrotas et al., 2018), altering lattice constants of the Sb_2S_3 , potentially explaining the discrepancy in bandgap observed between $\text{Sb}_2\text{S}_3\text{-N}_2$ and $\text{Sb}_2\text{S}_3\text{-air}$ films.

To investigate the chemical composition differences between $\text{Sb}_2\text{S}_3\text{-air}$ and $\text{Sb}_2\text{S}_3\text{-N}_2$ films, X-ray photoelectron spectroscopy (XPS) was carried out. The Sb 3d spectra of $\text{Sb}_2\text{S}_3\text{-N}_2$ and $\text{Sb}_2\text{S}_3\text{-air}$ films are illustrated in Fig. 4a and c, respectively. The $\text{Sb}_2\text{S}_3\text{-Air}$ film exhibits double peaks at 528.5 eV and 537.9 eV, which are attributed to Sb 3d_{5/2} and Sb 3d_{3/2}, respectively, originating from the Sb-S bond (Jiang et al., 2019). Additional peaks at 529.7 eV and 539.1 eV are identified as the

Table 2

Photovoltaic average of solar cells fabricated with $\text{Sb}_2\text{S}_3\text{-air}$ and $\text{Sb}_2\text{S}_3\text{-N}_2$ films measured under one Sun AM 1.5G illumination. In each condition, cell number = 5.

Device	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill Factor (%)	PCE (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
$\text{Sb}_2\text{S}_3\text{-air}$	0.31 $\pm$ 0.07	5.79 $\pm$ 0.23	31.49 $\pm$ 3.94	0.57 $\pm$ 0.26	31.50 $\pm$ 2.82	85.26 $\pm$ 3.14
$\text{Sb}_2\text{S}_3\text{-N}_2$	0.49 $\pm$ 0.058	6.67 $\pm$ 0.35	32.63 $\pm$ 2.36	1.07 $\pm$ 0.16	50.67 $\pm$ 2.81	102.41 $\pm$ 2.94

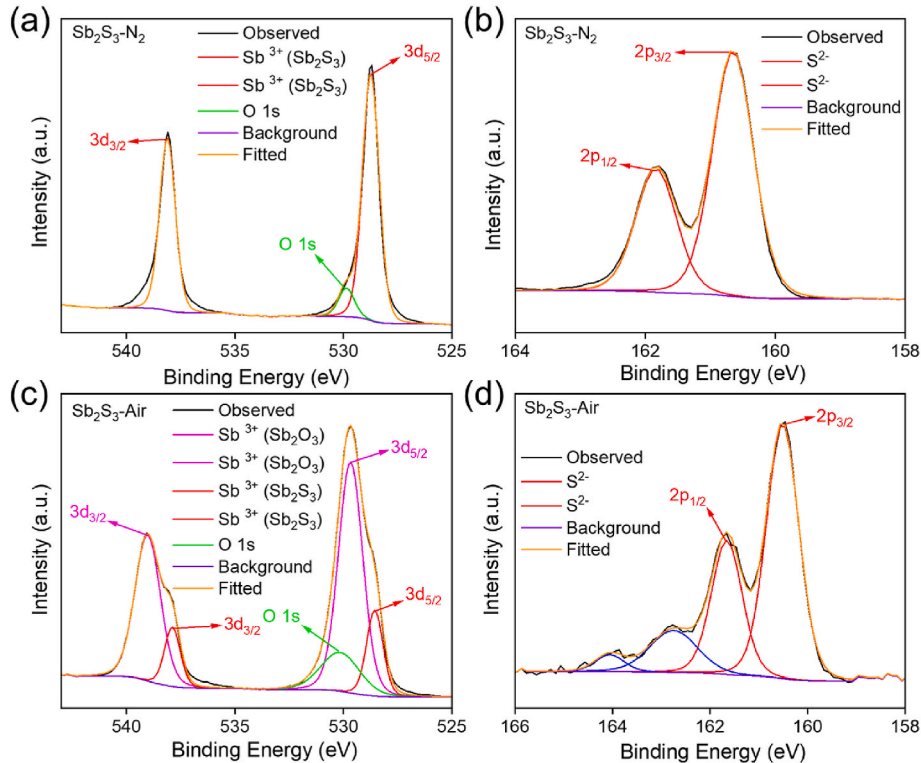


Fig. 4. Chemical composition of $\text{Sb}_2\text{S}_3\text{-air}$ and $\text{Sb}_2\text{S}_3\text{-N}_2$ films. High-resolution X-Ray photoelectron spectroscopy (XPS) spectra of (a), Sb 3d and (b), S 2p peaks of $\text{Sb}_2\text{S}_3\text{-N}_2$ film. (c), Sb 3d and (d), S 2p peaks of $\text{Sb}_2\text{S}_3\text{-air}$ film.

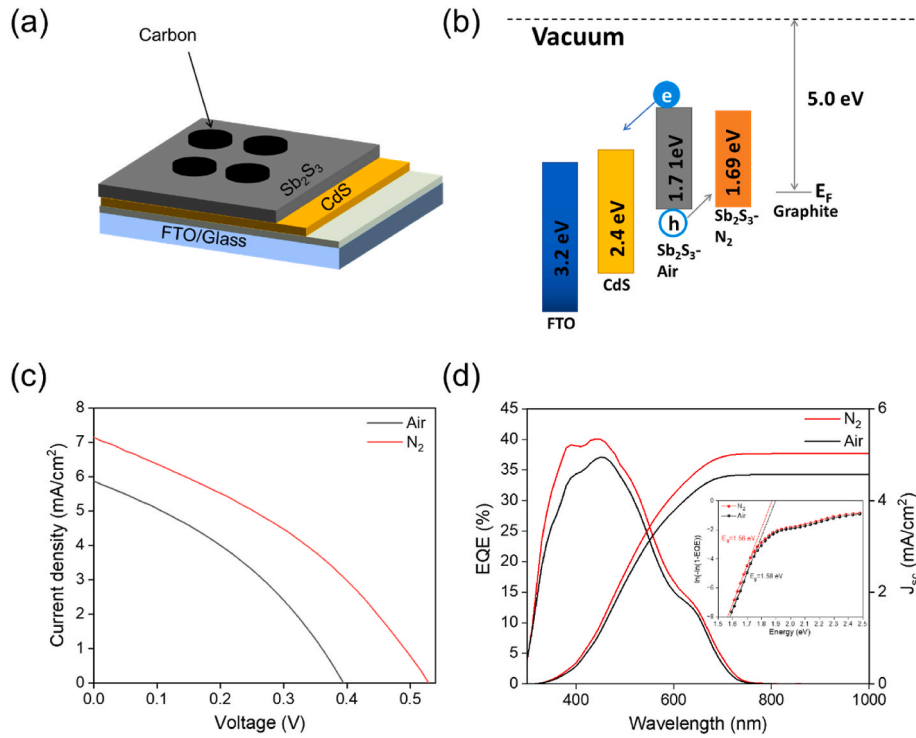


Fig. 5. Device configuration and device performance characterizations. (a), Schematics of a typical device structure. (b), Energy level band alignment of the device. (c), Current density-voltage curves and (d), external quantum efficiency (EQE) spectra of devices fabricated with Sb_2S_3 -air and Sb_2S_3 - N_2 films. Inset figure illustrates the bandgap derived from the EQE spectra of the devices.

Sb-O band, suggesting the presence of Sb_2O_3 in the Sb_2S_3 -Air film (Han et al., 2020). The S 2p peak fitting displays two peaks located at a binding energy of 160.6 eV and 161.8 eV, corresponding to $2p_{3/2}$ and $2p_{1/2}$, respectively, for both Sb_2S_3 -air and Sb_2S_3 - N_2 films (Jiang et al., 2019). The formation of Sb_2O_3 in the Sb_2S_3 -air film may result from the presence of dissolved oxygen in the precursor, given that both the Sb_2S_3 -air film and Sb_2S_3 - N_2 film were annealed in the dry N_2 -filled glovebox. This observation provides evidence that the formation of Sb_2S_3 film is sensitive to the precursor fabrication conditions.

To understand how grain engineering impacts the electrical behavior in Sb_2S_3 film-based solar cells, we fabricated simple solar cell devices using both Sb_2S_3 -Air and the Sb_2S_3 - N_2 films (see Table 2). Note that the device architecture was simplified to FTO/CdS/ Sb_2S_3 /Carbon electrode, as shown in Fig. 5a. The band alignment for the device is displayed in Fig. 5b (Guo et al., 2019), where the bandgap of the Sb_2S_3 -air and Sb_2S_3 - N_2 films differs, potentially leading to various carrier extraction. Current density-voltage (J-V) curves under one Sun AM 1.5G illumination are presented in Fig. 5c. Detailed device performance of solar cells fabricated with the Sb_2S_3 - N_2 and Sb_2S_3 -air films is listed in Table 2. The device fabricated with Sb_2S_3 - N_2 film exhibits a highest power conversion efficiency (PCE) of 1.35% with a V_{oc} of 0.54 V, J_{sc} of 7.14 mA/cm^2 , and a fill factor (FF) of 35.01%, while the device with Sb_2S_3 -air absorber demonstrates a highest PCE of 0.82%, a V_{oc} of 0.39 V, a J_{sc} of 5.87 mA/cm^2 , and an FF of 35.84%. The increase in V_{oc} and J_{sc} of the Sb_2S_3 - N_2 device can be associated with the pinhole-free morphology, as shown in Fig. 1. These pinholes on the Sb_2S_3 -air film may act as recombination centers, negatively impacting device performance due to direct contact between the back contact and electron transport layer (Zhang et al., 2023). Additionally, the larger grain size of the Sb_2S_3 - N_2 film may also reduce the grain boundary density and consequently reduce carrier recombination in the film (Kim et al., 2016). Moreover, $(\text{Sb}_4\text{Se}_6)_n$ nanoribbons grown with (hkl) planes may also facilitate carrier transport along the ribbons, promoting the improved device performance (Zhou et al., 2015; Peng et al., 2023). However, the device fabricated with Sb_2S_3 - N_2 film exhibits a slightly lower FF, and enhanced

series resistance. While fewer pinholes are present in the Sb_2S_3 - N_2 film, the series resistance of the corresponding device increases, and the parallel resistance of the device increases. The direct contact between the buffer layer and the back contact, facilitated by pinholes in the absorber, could create current paths, potentially compromising device performance. However, the extent of loss paths depends on the combinations of buffer layer and back contact (Kaenung et al., 2018b). Therefore, passivating pinholes in the film may not ensure a significant enhancement in the fill factor of the device. External quantum efficiency (EQE) results in Fig. 5d illustrate that the device fabricated with Sb_2S_3 - N_2 film exhibits better photon response. The significantly lower current density observed in the EQE spectra compared to the I-V curves can be attributed to the different wavelength ranges between the AAA solar simulator for the IV and EQE measurements, and the rough interface between the light absorber and the porous carbon electrode (Amin et al., 2023; Dalal and Moore, 1977; Dalal and Rothwarf, 1979; 1). Bandgap was also determined from the EQE spectra and incorporated into the inset of Fig. 5d. According to the equation $\ln(-\ln(1-EQE)) \propto (E-E_g)/E_U$ (Li et al., 2019; Hages et al., 2016), where E_g represents the bandgap, the intercept with the X-axis corresponds to the bandgap. The bandgaps of the Sb_2S_3 -Air and Sb_2S_3 - N_2 films were 1.58 eV and 1.56 eV, respectively. Results from both EQE spectra and Tauc fitting indicate that the Sb_2S_3 -Air film exhibits a slightly larger bandgap. As a result, a blue shift was observed in the Sb_2S_3 -Air device in the EQE spectra compared to the Sb_2S_3 - N_2 device.

4. Conclusions

In summary, our work reveals that controlling oxygen during the precursor preparation step significantly influences the grain size, grain orientation, and chemical composition of Sb_2S_3 films, consequently impacting the performance of the corresponding solar cells. The Sb_2S_3 - N_2 film shows a larger grain size with a smooth surface, ensuring a better junction quality. Sb_2S_3 - N_2 film prefers (hkl) orientation, which is beneficial for carrier transport. Additionally, oxygen is introduced and

converted into the Sb_2O_3 during film annealing. Sb_2S_3 - N_2 solar cell exhibits a better PCE of 1.35%, which reflected the improved Sb_2S_3 film quality. Therefore, this work provides evidence that the control of oxygen in the Sb_2S_3 precursor significantly impacts the quality of the resulting Sb_2S_3 film. This study offers valuable insights into a novel approach for regulating grain engineering in Sb_2S_3 , leading to enhanced film quality. These findings hold significant promise for the development of highly efficient Sb_2S_3 solar cells.

CRedit authorship contribution statement

Xiaomeng Duan: Writing – original draft, Methodology. **Al Amin:** Writing – review & editing, Methodology. **Yizhao Wang:** Writing – review & editing. **Feng Yan:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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