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Preparation and characterization of SbSeI thin films



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ARTICLE INFO	ABSTRACT
Keywords: Antimony selenoiodide Pnictogen chalcohalides Thin films Photoluminescence SbSeI	Metal chalcohalides are promising candidates for next-generation technologies that include energy conversion, information storage, and quantum computing. Among them, antimony selenoiodide (SbSeI) has received rising interest for different optoelectronic devices, including photovoltaics, due to its bandgap energy, strong optical absorption, stability, and earth abundant, low-cost, and low toxicity constituents. In this work, SbSeI thin films were prepared through a two-step process. At first, antimony selenide (Sb_2Se_3) thin films were deposited at 300 °C (Sb_2Se_3-300) and at room temperature (Sb_2Se_3-RT) onto molybdenum covered soda-lime glass substrates by a magnetron sputtering method. The formation of SbSeI thin films was performed by isothermally annealing the as-deposited Sb_2Se_3 thin films in sealed quartz ampoules in the atmosphere of antimony iodide (SbI_3) with the presence of 100 Torr of argon pressure. The influence of the annealing temperature and time during the iodization of different types of substrates on the morphology and composition of SbSeI thin films was investigated. The well-oriented and dense single-phase SbSeI thin films with stoichiometric composition and single-crystal micro-columnar structures were achieved by annealing Sb_2Se_3-RT in SbI_3 atmosphere at 250 °C for 5 min under 100 Torr of Ar pressure. The room temperature photoluminescence (RT-PL) of SbSeI exhibited a broad asymmetric PL band at 1.4 eV, being quite distant from the bandgap. This PL band at 1.4 eV with obtained small thermal quenching activation energy of 12.7 meV is proposed to originate from the deep donor-deep acceptor pair (DD-DA) recombination.

1. Introduction

Emerging photovoltaic technologies, such as kesterite, Sbchalcogenide, dye-sensitized solar cells, organic solar cells, and perovskite solar cells, are currently under research as alternatives to traditional silicon solar cells [1]. Perovskites, among these candidates, exhibit exceptional optoelectronic properties [2]. Notably, Pb-based perovskite solar cells have already achieved a power conversion efficiency (PCE) of 25.7 % [3], making them very attractive for solar energy applications. Although remarkable progress has been made in the development of perovskite-based photovoltaic technology, the commercialization of these solar cells has significant limitations due to their instability and toxicity issues [4]. Exposure to humid conditions, heat or light tends to induce rapid degradation of perovskite materials [5]. Moreover, during the fabrication and operation of devices, Pb-perovskites have a tendency to decompose into components containing lead, posing potential environmental and health hazards [6]. Therefore, there is a critical need to explore and identify more stable and Pb-free materials that could be considered as promising alternatives to Pb-perovskites as an absorber layer in solar cell applications. Antimony selenide (Sb₂Se₃) solar cells have gained extensive research attention in recent years. While demonstrating enhanced stability compared to Pb-perovskites [7], Sb₂Se₃ solar cells suffer from a large open circuit voltage (V_{oc}) deficit associated with its complex defect chemistry. Despite recent efforts aimed at enhancing V_{oc} [8,9], the efficiency record of Sb₂Se₃ solar cells has reached around 10 % [10], leaving plenty of room for improvement considering the theoretical Shockley–Queisser (S-Q) limit for Sb₂Se₃, which stands at 30 %.

The defect tolerance observed in Pb-perovskites is closely related to the ns² electronic configuration of Pb²⁺ (5s²). Metallic cations like Sb³⁺ or Bi³⁺ share the same ns² electronic configuration, offering a high dielectric constant, low effective masses and anti-bonding character of

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the valence band. These properties collectively contribute to defecttolerant transport properties [11]. One potential group of materials displaying the ns² electronic configuration is metal chalcohalides. These compounds consist of a trivalent heavy pnictogen cation, a divalent chalcogenide and monovalent halide anions. They are typically represented by the general chemical formula MXY, where M = Bi or Sb; X = S, Se, or Te; and Y=Cl, Br, or I.

While heavy pnictogen chalcohalides have historically received less attention compared to other materials, there has been a recent surge in interest aim at exploring their potential as absorber materials in solar cells [12–17]. Among them, antimony selenoiodide (SbSeI) has received rising interest for different optoelectronic devices including photovoltaics [18,19]. SbSeI has an orthorhombic crystal structure with the space group *Pnma* 62 [20]. It has high absorption coefficient ($\sim 10^5$ cm⁻¹) and an indirect bandgap of 1.67 eV [21]. Theoretical calculations have shown that dominant defects in SbSeI are Se_I acceptors and I_{Se} donors, leading to an electrical conductivity that can only exhibit weak *n*-type or weak *p*-type characteristics [22]. Defects play a major role in determining the performance of photovoltaics and therefore careful investigation is needed.

SbSeI has been synthesized through different methods-by melting at high temperatures from elements in sealed ampoules [23], by the sonochemical method using pure elements [24] and by the Bridgman technique [25]. SbSeI thin films have been deposited using multiple techniques: from previously deposited antimony selenide (Sb₂Se₃), from an Ethane dithiol/Ethylene diamine solution followed by casting an antimony iodide (SbI₃) solution or thermal formation and then, by iodization of the Sb₂Se₃ with iodine vapors produced by heating iodine pellets in a closed gas chamber [26]. Nie et al. fabricated SbSeI-based solar cells by depositing SbSeI onto mesoporous titanium oxide (TiO₂) using multiple spin-coating cycles of SbI3 solutions onto Sb2Se3, previously formed through thermal decomposition and crystallization. These solar cells demonstrated remarkable stability regardless of humidity, temperature, and light, while achieving a power conversion efficiency of 4.1 % [18]. Although SbSeI has very promising properties, there are few studies where this material has been used as an absorber layer in solar cells, and the obtained efficiency is still far from the theoretical 28 % [25].

SbSeI crystallizes into the $(M_2X_2Y_2)_n$ double-chained system, that are covalently linked along the chain axis direction, while at out-of chainaxis directions, the adjacent chains are joined together by van der Waals forces. The pseudo-1D crystal structure of these materials and growth rate anisotropy can be problematic for the formation of dense thin films in a planar photovoltaic device [27]. On the other hand, the optimization of the grain orientation in materials with similar 1D crystal structure as Sb₂Se₃ has been proved critical to enhance the performance of solar cells [28,29]. Careful control of annealing parameters, such as temperature, pressure, and duration, significantly influences the characteristics of the resulting SbSeI films, including crystal structure, composition, and optical and electrical properties. Therefore, specific annealing conditions must be optimized to obtain SbSeI films with desirable properties for various applications.

The objective of this research is to fabricate SbSeI thin films using physical vapor transport to achieve homogeneous material with welloriented crystals, with the aim to obtain morphology and optoelectronic properties suitable for high-performance solar cells. In this work, SbSeI was prepared by iodizing sputtered Sb₂Se₃ thin films. The study investigates the influence of annealing temperature and time during the iodization on various types of substrates, exploring their impact on the morphology, composition, and optical properties of the resulting SbSeI thin films.

2. Experimental

2.1. Preparation of SbSeI thin films

Sb₂Se₃ thin films were deposited by radio frequency magnetron sputtering from Sb₂Se₃ target onto molybdenum covered soda-lime glass substrate. The thickness of the 800 nm Sb₂Se₃ thin films was adjusted by the sputtering time. The formation of SbSeI thin films was carried out by isothermal annealing of as-deposited Sb₂Se₃ thin films in sealed quartz ampoules in the SbI3 atmosphere. In this study, two different types of Sb₂Se₃ thin films were used: 1) sputtered at a substrate temperature of 300 °C (hereafter referred to as samples Sb₂Se₃-300), and 2) sputtered at a substrate temperature of 25 °C (hereafter referred to as samples Sb₂Se₃-RT). The used SbI₃ compound was self-synthesized isothermally in evacuated quartz ampoule. Sb₂Se₃ thin film substrates and a piece of SbI₃ were introduced into quartz ampoules. Then ampoules were degassed under dynamic vacuum, filled with 100 Torr of argon (Ar), sealed, and heated isothermally at different temperatures and time periods. For Sb₂Se₃-300 substrates, the iodization process was carried out at annealing temperatures from 150 to 350 °C for 1–20 min. For Sb₂Se₃-RT substrates, the iodization process was carried out at annealing temperatures of 200, 225 and 250 °C for 5 min.

2.2. Characterization

The morphology of the SbSeI thin films was characterized by a highresolution scanning electron microscope (HR-SEM Zeiss Merlin), equipped with a high-efficiency In-lens secondary electron detector for high-contrast surface imaging and an energy-selective backscattered electrons detector for compositional contrast. The chemical composition of the deposited SbSeI thin films was analyzed by energy dispersive Xray spectroscopy (EDX) on a Bruker Esprit 1.82 EDX system equipped with an EDX-XFlash 3001 detector with an accelerating voltage of 20 kV. The crystal structure of the formed SbSeI thin films was characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer at 40 kV and 40 mA operating with the silicon strip detector D/teX Ultra with monochromatic Cu K α ($\lambda = 1.5406$ Å) radiation. Phase analysis and lattice parameters were calculated by using PDXL2 Rigaku's software. Room temperature micro-Raman spectroscopy was used to determine the phase composition of SbSeI thin films. Raman spectra were recorded by a Horiba LabRam HR 800 spectrometer equipped with a multichannel CCD detection system in the backscattering configuration. A laser with wavelength 532 nm with a power intensity of 0.42 mW was used. The same equipment was used to perform the room temperature microphotoluminescence (RT-PL) measurements in visible spectral region. Ultraviolet-Visible-Near-Infrared (UV-Vis-NIR) Spectrophotometer Cary5000 was used to obtain the optical diffuse reflectance spectra of SbSeI thin films at room temperature. Measurements were recorded between 400 and 1100 nm. For temperature dependent PL measurements, the samples were mounted on the cold finger of the closed-cycle helium cryostat (Janis CCS-150) and cooled down to 8 K. The temperature was adjusted up to 80 K via a temperature controller (LakeShore Model 335). The Cobolt 08-DPL laser with a wavelength of 532 nm was used for PL excitation. The power of the incident laser beam was altered via neutral density filters between 0.04 and 0.37 mW. An optical chopper was used for modulating the laser light. The emitted light was conditioned using a cut-off low-pass filter and focused on the computercontrolled single grating (600 lines/mm) monochromator (f = 0.64 m) (Horiba Jobin Yvon FHR640). Luminescence was dispersed by the monochromator and detected by the R632 photomultiplier tube. Stanford SR810 DSP lock-in amplifier was used for amplifying the PL signal.

3. Results and discussion

3.1. Effect of annealing time and temperature on the Sb₂Se₃-300 morphology and composition

The morphology of iodized Sb_2Se_3 thin films was investigated as a function of the growth temperature and time. In this part of the study, the Sb_2Se_3 -300 substrates with crystalline structure were used (see Fig. 1).

Fig. 2 a-c show the SEM images of SbSeI thin films formed by iodization of Sb₂Se₃-300 at 150 °C. SEM analysis showed significant changes in the morphology of formed SbSeI thin films depending on annealing temperature and time. The thin films iodized at 150 °C for 5–20 min (Fig. 2a–c) consist of SbSeI micro-columns. The length, thickness, and density of these columns increase with the annealing time. Nevertheless, regardless of the heating duration, all films exhibited a layer of unreacted Sb₂Se₃ beneath the layer of these micro-columns. This suggests that the annealing temperature of 150 °C is not enough for the complete formation of a single phase SbSeI thin film.

Elevating the growth temperature to 175 °C accelerates the reaction between Sb₂Se₃ with SbI₃, leading to the formation of regularly shaped micro-columnar crystals with length of 5–6 µm (Fig. 3a–c) regardless of annealing time (5–20 min). Nevertheless, the bottom of the film consists of smaller grains with a porous structure, indicating the present of unreacted Sb₂Se₃. A similar layer was also seen after annealing for 20 min at 175 °C (see Fig. 3c).

Annealing at higher temperatures (≥ 200 °C) for shorter times (3 min) resulted also in the formation of double layer structure of the thin films. For example, Fig. 4a and b shows the cross-sectional SEM images after annealing for 3 min at 225 °C and at 300 °C, respectively. Increasing the reaction duration to 5 min at annealing temperature 200–300 °C, results in complete formation of SbSeI thin films. Although the double-layer structure remines, but both layers contain only SbSeI phase (see Fig. 5a–c). At an annealing temperature of 350 °C, the formation of micro-columnar crystals stopped, and instead a non-uniform, irregular and flat SbSeI layer was observed.

The cross-sectional SEM images of the SbSeI thin film revealed that the thickness of the films increased with the annealing temperature as the length of the micro-columnar crystals increased. After annealing at 300 °C for 5 min, the length of the crystals increased to ~37 μ m. In comparison, the initial thickness of the Sb₂Se₃ film was ~0.8 μ m (see Fig. 1b). Not only the length but also the diameter of the SbSeI micro-columns depended on the annealing temperature. Micro-columnar crystals with a diameter of ~500 nm and a length of ~17 μ m were formed by annealing at 250 °C for 5 min, while annealing at 300 °C for 5 min results in crystals with a diameter of ~2 μ m. In the latter case, the thin film morphology was non-uniform, the random distribution of thicker micro-columnar with sharp needles can also be seen in Fig. 5c. With a further increase in the annealing temperature to 350 °C and higher, the micro-columnar crystals were no longer formed, and instead a non-uniform, irregular and flat SbSeI layer was observed.

According to EDX analysis (Table 1), the chemical composition of the formed thin films is strongly influenced by the annealing temperature and time. At lower temperatures (150 °C for t = 5–20 min and 175 °C for t = 5–10 min), the resulting films were iodine poor. The deficiency of iodine was also detected in the samples that were annealed for shorter times at temperature 225 °C (t = 1–3 min), 250 °C (t = 1–3 min) and 300 °C (t = 1 min). This result indicates an unreacted Sb₂Se₃ layer that was also seen in SEM images in Figs. 3 and 4. EDX analysis showed that film annealed at temperature 175 °C (t = 15–20 min) and 300 °C (t = 3-5 min) had Sb-rich and I-rich composition. This could be attributed to coexistence of the SbI₃ phase alongside the main SbSeI compound. SbSeI thin films with composition close to stoichiometry (Sb: Se: I = 1 : 1: 1) formed by annealing Sb₂Se₃ films in SbI₃ at 100 Torr of Ar atmosphere for 5 min within the temperature range of 200–250 °C.

Raman spectroscopy analysis was carried out to investigate the phase composition of the thin films and to confirm the presence of possible secondary phases proposed by EDX. Raman spectra of as-deposited Sb₂Se₃, and after annealing at 150, 175 and 200 °C for 5 min are shown in Fig. 6. All Raman spectra were fitted using Lorentzian functions to resolve the peaks. The Raman spectrum of as-deposited Sb₂Se₃ showed a dominating peak at 190 cm^{-1} and less intense peaks at 99, 124, 154 and 212 cm⁻¹ (see Fig. 6a). These Raman frequencies are attributed to Sb₂Se₃ and are in good correlation with the literature [30]. The fitting results of the Raman spectrum of the thin film, annealed at 150 °C for 5 min (Fig. 6b), revealed peaks at 95, 116, 137, 165, 184, 209, 211, 233, 237 and 255 cm⁻¹ showing the mixture of different phases. The peaks at 211 cm⁻¹ and 255 cm⁻¹ could be attributed to the Sb₂Se₃ [31] and Sb₂O₃ [32], respectively. The origin of the Sb₂O₃ formation could be due to the sensitivity of the Sb-containing compounds to the potential photo-induced transformation or degradation during the Raman measurements [32,33]. The most intensive peaks at 233 and 237 cm⁻¹ belong to the trigonal Se [34]. The Raman spectrum of the thin film annealed for 5 min at 200 °C (Fig. 6d), exhibited peaks at 95, 116, 137, 165, 184, 209, and 214 cm^{-1} . The identified peaks are characteristic to SbSeI and have been previously reported in the literature [26, 35]. Peaks below 200 cm⁻¹ are assigned to Sb–I bonds and 209 cm⁻¹ is assigned to the Sb-Se heteropolar vibration [26,36]. The Raman spectrum analysis of the film annealed at 175 °C (Fig. 6c) revealed, in addition to the SbSeI peaks, the presence of weaker peaks at 233, 237 and 255 cm^{-1} (attributed to Se and Sb₂O₃), which indicates non-uniform growth of SbSeI crystals. The SbSeI layers formed at 150 °C and 175 °C, exhibited higher sensitivity to the laser power of Raman equipment when compared to the sample prepared at 200 °C. This is probably due to the incomplete reactions in the Sb₂Se₃ + SbI₃ system. All Raman analysis results are in a good correlation with the data presented in Table 1 and confirm the presence of secondary phases at annealing temperatures lower than 200 °C. Annealing the thin films at temperatures higher than 200 °C (up to 300 °C) for 5 min resulted in unchanged positions of the Raman peaks (spectra not presented here). However, there was observed increase in the intensity ratio of the peaks at 95 and 209 cm^{-1} compared to the other peaks.



Fig. 1. SEM images of a) top view and b) cross-section of Sb₂Se₃ thin film sputtered at 300 °C.



Fig. 2. SEM images of cross-section and surface of SbSeI thin films annealed in SbI3 and 100 Torr of Ar atmosphere at 150 °C for a) 5, b) 10, and c) 20 min.



Fig. 3. SEM images of cross-section and surface of SbSeI thin films annealed in SbI3 and 100 Torr of Ar atmosphere at 175 °C for a) 5, b) 10, and c) 20 min.



Fig. 4. SEM images of cross-section of SbSeI thin films annealed in SbI₃ and 100 Torr of Ar atmosphere: a) at 225 °C for 3 min and b) at 300 °C for 3 min.



Fig. 5. SEM images of cross-section and surface of SbSeI thin films annealed in SbI_3 and 100 Torr of Ar atmosphere during 5 min at a) 200 °C. b) 250 °C and c) 300 °C.

Table 1
Chemical composition of SbSeI thin films annealed at different temperatures and
times measured by EDX.

Annealing	Annealing	Sb, at	Se, at	I, at	Proposed
temperature, °C	time, min	%	%	%	phases
150	5	35.2	55.2	9.6	SbSeI,
					Sb ₂ Se ₃ , Se
	10	36.8	48.2	15.0	SbSeI,
					Sb ₂ Se ₃ ,
	15	36.9	46.5	17.6	SbSeI,
					Sb ₂ Se ₃
	20	35.4	51.4	13.3	SbSeI,
					Sb ₂ Se ₃ , Se
175	5	36.7	36.9	26.4	SbSeI,
					Sb ₂ Se ₃
	10	36.0	37.4	26.6	SbSeI,
					Sb ₂ Se ₃
	15	35.2	30.1	34.7	SbSeI, SbI ₃
	20	37.0	27.9	35.2	SbSeI, SbI ₃
200	5	34.5	32.6	32.9	SbSeI
	10	36.6	37.1	26.4	SbSeI,
					Sb ₂ Se ₃
	15	37.8	38.7	23.5	SbSeI,
					Sb ₂ Se ₃
225	1	36.6	57.7	5.7	SbSeI,
					Sb ₂ Se ₃ , Se
	3	35.4	35.3	29.3	SbSeI,
					Sb ₂ Se ₃
	5	34.2	32.7	33.1	SbSeI
250	1	37.1	55.0	8.0	SbSeI,
					Sb ₂ Se ₃ , Se
	3	35.9	33.8	30.2	SbSeI,
					Sb ₂ Se ₃
	5	34.1	32.8	33.1	SbSeI
300	1	39.3	48.8	11.9	SbSeI,
					Sb ₂ Se ₃
	3	34.7	29.7	35.6	SbSeI, SbI ₃
	5	34.4	29.7	35.9	SbSeI, SbI ₃



In summary, the single layer micro-columnar structured SbSeI films with stoichiometric composition were obtained by annealing Sb₂Se₃-300 in SbI₃ atmosphere at 200–250 °C for 5 min under 100 Torr of Ar pressure. However, the thin film layer consisted of randomly oriented and not tightly packed crystals. Most probably, the orientation of the asdeposited Sb₂Se₃-300 thin film crystals determines the properties of the

Fig. 6. RT Raman spectra of: a) Sb_2Se_3 sputtered at 300 $^\circ C$ and SbSeI annealed at b) 150, c) 175 and d) 200 $^\circ C$ respectively for 5 min under 100 Torr of Ar pressure.

formed SbSeI.

3.2. Effect of annealing temperature on the Sb_2Se_3 -RT morphology and composition

To improve the alignment and packing density of the SbSeI thin film crystals, amorphous Sb₂Se₃ substrates (sputtered at RT) were used. SEM images of the cross-section and top view of an amorphous Sb₂Se₃ substrates is shown in Fig. 7. Based on the knowledge gathered from previous experimental series, the Sb₂Se₃-RT films were annealed in SbI₃ atmosphere at temperatures of 200, 225 and 250 °C for 5 min under 100 Torr of Ar pressure.

Fig. 8 shows SEM images of cross-section and top-view of the formed SbSeI thin films after iodization of Sb₂Se₃-RT at temperature ranging from 200 to 250 °C for 5 min. According to SEM studies, annealing at 200–225 °C for 5 min led to an ununiform double layer structure comprising unreacted Sb₂Se₃-RT and SbSeI crystals that exhibited irregularities in length, thickness, and orientation, as shown in Fig. 8a and b. At a temperature of 250 °C, a uniform thin film characterized by well-oriented, densely packed, and micro-columnar structured crystals was successfully obtained, as seen in Fig. 8c. Under these conditions, no unreacted antimony selenide was detected. The EDX analysis revealed that the chemical composition of formed SbSeI thin film is Sb- and I-rich, suggesting the presence of SbI₃. The atomic percentage ratio of Sb:Se:I was determined to be 35.2:29.7:35.1 (at%).

The phase composition and crystal structure of the SbSeI thin films formed at 250 °C were investigated by Raman spectroscopy and XRD (Fig. 9a and b). In Fig. 9a, the Raman spectra of the SbSeI show distinct peaks at 96, 117, 138, 168, 180, 209, and 214 cm⁻¹, which are attributed to SbSeI phase [26,35]. The Raman spectra of the thin films did not reveal the presence of secondary phases. The width of Raman peak is an indicator of the crystallinity and structural distribution, with crystalline materials exhibiting sharper and narrower Raman peaks compared to amorphous materials. For the SbSeI thin film, formed through the annealing process of Sb₂Se₃-RT at 250 °C for 5 min in SbI₃ atmosphere under 100 Torr of Ar pressure, the Raman peaks were sharper and narrower in comparison to other produced thin films. This indicates a higher level of crystallinity within the SbSeI structure. The full width at half maximum (FWHM) of the main Raman peak at 209 cm⁻¹ is 3.82 cm⁻¹.

In Fig. 9b, the XRD pattern of the SbSeI thin film crystals formed by annealing of Sb₂Se₃-RT at 250 °C for 5 min is shown. According to XRD pattern, the SbSeI film consists of orthorhombic crystal structure of SbSeI phase with the space group Pnma 62 (ICSD 01-076-1354) as the primary phase. Additionally, there is a presence of SbI₃, identified as a minor secondary phase (diffraction peak at $2\theta = 36.5^{\circ}$). Furthermore, the sharp peak at $2\theta = 40.6^{\circ}$ corresponds to the (110) reflection of the Mo substrate. The determined lattice parameters for SbSeI *a* = 8.671 Å, *b* = 4.118 Å and *c* = 10.382 Å are in good agreement with the literature data [37]. Two strong and sharp reflections at 2θ angles of 29.4° (112) and 43.9° (020) reveal that the SbSeI crystals have two preferred orientations. It is also seen in SEM image of SbSeI thin film (Fig. 8c top

view) that some crystals are grown horizontally on top of the well-oriented vertical crystals. Further research is needed to develop a growth methodology for highly c-axis-oriented SbSeI thin films with (112) reflections.

3.3. Characterization of SbSeI thin films' optical properties

UV–Vis spectroscopy is a widely used technique to determine the optical bandgap of thin film materials. The Kubelka-Munk theory is commonly used to evaluate the optical bandgap from reflectance spectra [38,39]. The reflectance spectra of the SbSeI thin film after using Kubelka-Munk function are shown in Fig. 10a. By extrapolating the linear least squares fit of $[F(R_{\infty})h\nu]^2$ versus $h\nu$ using linear fitting, where R_{∞} is absolute diffuse reflectance, h is the Plank's constant and ν is the photon frequency, estimated direct optical bandgap was found to be 1.72 eV. This value is consistent with previously reported value [40].

Optical properties of SbSeI thin films were characterized by RT-PL and LT-PL. In Fig. 10b, the RT-PL spectrum of SbSeI shows a broad asymmetric band with a maximum around 1.67 eV.

In Fig. 11a and b, the dependence of low-temperature PL emission on laser power and temperature is presented, respectively. PL observations at low temperatures show a broad and asymmetric PL band at roughly 1.4 eV.

Unfortunately, we were unable to measure the entire PL spectrum because of the detector sensitivity limitation. Despite this, we can see that the peak position of the PL band exhibits a noticeable redshift as temperature increases. This shift can be attributed to the temperature dependence of the bandgap energy. Additionally, a minor blueshift is observed with increasing laser power. The measurement system created a spectral characteristic at about 1.32 eV, which made it more challenging to pinpoint the peak position at higher temperatures. According to the power law $\sim P^m$, where *P* is the excitation power and *m* is the exponent, the excitation power dependence of the intensity of the integrated PL band is shown in Fig. 12a. The linear fitting enabled the extraction of the *m* value, indicating the type of recombination, and resulted in a value of 1.2. Usually, excitonic or band-to-band emission is associated with these high exponent values [41].

The temperature dependence of the PL band showed very fast quenching. The thermal activation energy for this band was obtained from the Arrhenius plot (Fig. 12b), where the dependence of $\ln(\Phi)$ versus 1000/T was fitted by using a theoretical expression for discrete energy levels [42]:

$$\Phi(T) = \Phi_0 / \left(1 + \alpha_1 T^{3/2} + \alpha_2 T^{3/2} \exp(-E_a / kT) \right)$$
(1)

where Φ is integrated PL intensity, α_1 and α_2 are the process rate parameters and E_a is the thermal activation energy. As predicted by the fast quenching of the PL spectra with temperature, very small thermal activation energy for the PL band was obtained, see Fig. 12b. Considering the room temperature band gap of SbSeI ($E_g = 1.72 \text{ eV}$) [18], the observed PL band position at T = 8 K appears significantly distant from the band gap. The obtained small thermal activation energy of 12.7 meV



Fig. 7. SEM images of a) top view and b) cross-section of Sb₂Se₃ thin film sputtered at room temperature.



Fig. 8. SEM images of cross-section and surface of SbSeI thin films annealed in SbI_3 and 100 Torr of Ar atmosphere during 5 min at a) 200 °C. b) 225 °C and c) 250 °C.



Fig. 9. a) RT Raman spectra and b) XRD pattern of SbSeI thin film formed by annealing Sb₂Se₃-RT at 250 °C for 5 min in SbI₃ atmosphere under 100 Torr of Ar pressure.



Fig. 10. a) Calculation of the optical bandgap from extrapolation of the linear least squares fit of $[F(R_{\infty})h\upsilon]^2$ vs h υ using linear fitting in the Tauc representation of SbSeI. Experimental data (black line); fitted range (red line). b) Room temperature photoluminescence spectrum of the SbSeI thin film (black line). Experimental data was fitted using SplitVoigt function (red line).

may suggest that the PL band at 1.4 eV possibly originates from the recombination of a deep donor-deep acceptor pair (DD-DA) [43,44]. The same model was also suggested for the PL bands in polycrystalline Sb₂Se₃ [30].

from a donor-acceptor pair that is separated from one another by a distance r [45]:

$$h\nu_{max} = E_g - (E_a + E_d) + \frac{e^2}{4\pi\varepsilon_0\varepsilon r}$$
(2)

The following equation can be used to determine the emission energy



Fig. 11. a) Laser power dependence and b) temperature dependence of deep PL band.



Fig. 12. a) Integral PL intensity versus laser power. The fitting result is given as a black line; b) temperature dependence of integral intensity, the fitting result with Eq. (1) is given as a black curve.

where E_g is the bandgap energy, E_a and E_d are the ionization energies of the acceptor and donor, respectively, r is the distance between the donor and acceptor, e is the electron charge, ε is the static dielectric constant, and ε_0 is the permittivity of the vacuum. The Coulomb interaction between the donor and acceptor defects is described in Eq. (2)'s last term. The deep donor (acceptor) level's electron (hole) wave function is very confined. Therefore, only very close donor-acceptor pairs can show recombination due to overlapping of carries wave function. When single acceptor and donor defect levels are coupled, they tend to shift closer to the band boundaries. Consequently, the thermal activation energy associated with these complexes decreases significantly. As outlined in Ref. [46], it has been observed that when the laser power is increased, the PL intensity, particularly in case of DD-DA pairs, demonstrates a near-linear increase. Future research is required to fully understand the characteristics of this deep PL band.

4. Conclusions

In the present work, SbSeI thin films were prepared through a twostep process. Sb₂Se₃ thin films, prepared via sputtering at 300 °C and RT, were iodized isothermally within sealed quartz ampoules in the SbI₃ atmosphere under 100 Torr of argon pressure. The investigation focused on understanding the influence of technological parameters—specifically, annealing temperature and duration—during the iodization process involving various substrate types. The aim was to evaluate their impact on the morphology, composition, structural, and optical properties of the obtained SbSeI thin films. EDX and SEM analyses indicated a significant correlation between the chemical composition and the morphology of formed thin films with the annealing temperature, time and the initial Sb₂Se₃ thin film substrate used. Achieving well-oriented, dense SbSeI thin films with stoichiometric composition and singlecrystal micro-columnar structures was successful by annealing Sb₂Se₃-RT in SbI₃ atmosphere at 250 °C for 5 min. Raman and XRD analysis confirmed the formation of mainly single-phase high crystallinity SbSeI. The direct band gap energy value of 1.72 eV was determined by UV–Vis spectroscopy. The room-temperature PL of SbSeI exhibited a broad asymmetric PL band with a maximum at around 1.67 eV. The low-temperature (T = 8 K) PL analysis revealed a distinct broad and asymmetric PL band at 1.4 eV, being quite distant from the bandgap. This PL band at 1.4 eV, coupled with a low thermal quenching activation energy of 12.7 meV, is proposed to originate from the deep donor-deep acceptor pair recombination.

CRediT authorship contribution statement

Marc Dolcet Sadurni: Methodology, Writing – original draft, Data curation, Investigation, Formal analysis. Kristi Timmo: Supervision, Project administration, Writing – review & editing, Investigation, Data curation, Formal analysis. Valdek Mikli: Investigation, Formal analysis. Olga Volobujeva: Investigation, Resources. Idil Mengu: Investigation, Formal analysis. Jüri Krustok: Writing – review & editing, Investigation, Formal analysis. Maarja Grossberg-Kuusk: Funding acquisition. Marit Kauk-Kuusik: Supervision, Project administration, Writing – review & editing, Funding acquisition.

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.

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References

- M. Giannouli, Current status of emerging PV technologies: a comparative study of dye-sensitized, organic, and perovskite solar cells, Int. J. Photoenergy 2021 (2021) 1–19, https://doi.org/10.1155/2021/6692858.
- [2] A.K. Jena, A. Kulkarni, T. Miyasaka, Halide perovskite photovoltaics: background, status, and future prospects, Chem. Rev. 119 (2019) 3036–3103, https://doi.org/ 10.1021/acs.chemrev.8b00539.
- [3] H. Min, D.Y. Lee, J. Kim, G. Kim, K.S. Lee, J. Kim, M.J. Paik, Y.K. Kim, K.S. Kim, M. G. Kim, T.J. Shin, S. Il Seok, Perovskite solar cells with atomically coherent interlayers on SnO₂ electrodes, Nature 598 (2021) 444–450, https://doi.org/10.1038/s41586-021-03964-8.
- [4] A. Babayigit, A. Ethirajan, M. Muller, B. Conings, Toxicity of organometal halide perovskite solar cells, Nat. Mater. 15 (2016) 247–251, https://doi.org/10.1038/ nmat4572.
- [5] D. Zhang, D. Li, Y. Hu, A. Mei, H. Han, Degradation pathways in perovskite solar cells and how to meet international standards, Commun. Mater. 3 (2022), https:// doi.org/10.1038/s43246-022-00281-z.
- [6] M. Ren, X. Qian, Y. Chen, T. Wang, Y. Zhao, Potential lead toxicity and leakage issues on lead halide perovskite photovoltaics, J. Hazard Mater. 426 (2022) 127848, https://doi.org/10.1016/j.jhazmat.2021.127848.
- [7] R. Tang, Z.H. Zheng, Z.H. Su, X.J. Li, Y.D. Wei, X.H. Zhang, Y.Q. Fu, J.T. Luo, P. Fan, G.X. Liang, Highly efficient and stable planar heterojunction solar cell based on sputtered and post-selenized Sb₂Se₃ thin film, Nano Energy 64 (2019) 103929, https://doi.org/10.1016/j.nanoen.2019.103929.
- [8] R. Tang, S. Chen, Z.H. Zheng, Z.H. Su, J.T. Luo, P. Fan, X.H. Zhang, J. Tang, G. X. Liang, Heterojunction annealing enabling record open-circuit voltage in antimony triselenide solar cells, Adv. Mater. 34 (2022) 1–11, https://doi.org/10.1002/adma.202109078.
- [9] G. Liang, M. Chen, M. Ishaq, X. Li, R. Tang, Z. Zheng, Z. Su, P. Fan, X. Zhang, S. Chen, Crystal growth promotion and defects healing enable minimum opencircuit voltage deficit in antimony selenide solar cells, Adv. Sci. 9 (2022) 1–15, https://doi.org/10.1002/advs.202105142.
- [10] Y. Zhao, S. Wang, C. Li, B. Che, X. Chen, H. Chen, R. Tang, X. Wang, G. Chen, T. Wang, J. Gong, T. Chen, X. Xiao, J. Li, Regulating deposition kinetics via a novel additive-assisted chemical bath deposition technology enables fabrication of 10.57%-efficiency Sb₂Se₃ solar cells, Energy Environ. Sci. 15 (2022) 5118–5128, https://doi.org/10.1039/d2ee02261c.
- [11] R.E. Brandt, V. Stevanović, D.S. Ginley, T. Buonassisi, Identifying defect-tolerant semiconductors with high minority-carrier lifetimes: beyond hybrid lead halide perovskites, MRS Commun 5 (2015) 265–275, https://doi.org/10.1557/ mrc.2015.26.
- [12] Y.C. Choi, R. Nie, Heavy pnictogen chalcohalides for efficient, stable, and environmentally friendly solar cell applications, Nanotechnology 34 (2023) 142001, https://doi.org/10.1088/1361-6528/acb05d.
- [13] U.V. Ghorpade, M.P. Suryawanshi, M.A. Green, T. Wu, X. Hao, K.M. Ryan, Emerging chalcohalide materials for energy applications, Chem. Rev. 123 (2023) 327–378, https://doi.org/10.1021/acs.chemrev.2c00422.
- [14] R. Nie, K.S. Lee, M. Hu, M.J. Paik, S. Il Seok, Heteroleptic tin-antimony sulfoidide for stable and lead-free solar cells, Matter 3 (2020) 1701–1713, https://doi.org/ 10.1016/j.matt.2020.08.020.
- [15] R. Nie, B. Kim, S.T. Hong, S. Il Seok, Nanostructured heterojunction solar cells based on Pb2sbs2l3: linking lead halide perovskites and metal chalcogenides, ACS Energy Lett. 3 (2018) 2376–2382, https://doi.org/10.1021/ acsenergylett.8b01332.
- [16] R. Nie, H.S. Yun, M.J. Paik, A. Mehta, B.W. Park, Y.C. Choi, S. Il Seok, Efficient solar cells based on light-harvesting antimony sulfoiodide, Adv. Energy Mater. 8 (2018) 1–7, https://doi.org/10.1002/aenm.201701901.
- [17] R. Nie, J. Im, S. Il Seok, Efficient solar cells employing light-harvesting Sb_{0.67}Bi_{0.33}SI, Adv. Mater. 31 (2019) 1–8, https://doi.org/10.1002/ adma.201808344.
- [18] R. Nie, M. Hu, A.M. Risqi, Z. Li, S. Il Seok, Efficient and stable antimony selenoiodide solar cells, Adv. Sci. 8 (2021) 1–8, https://doi.org/10.1002/ advs.202003172.
- [19] I. Caño, A. Navarro-Güell, E. Maggi, M. Barrio, J.L. Tamarit, S. Svatek, E. Antolín, S. Yan, E. Barrena, B. Galiana, M. Placidi, J. Puigdollers, E. Saucedo, SbSel and SbSeBr micro-columnar solar cells by a novel high pressure-based synthesis process, J. Mater. Chem. A (2023) 17616–17627, https://doi.org/10.1039/ d3ta03179a.
- [20] P.I. Rentzeperis, Crystal growth and structure of chalcohalogenides and chalcogenides of the general formulae $A_m^V B_n^{VI} C_p^{VI}$ and A_2B_3 with A = As, Sb, Bi; B = S, Se, Te and C = Cl, Br, I, Prog. Cryst. Growth Char. Mater. 21 (1991) 113–138, https://doi.org/10.1016/0960-8974(91)90010-A.
- [21] E. Wlaźlak, A. Blachecki, M. Bisztyga-Szklarz, S. Klejna, T. Mazur, K. Mech, K. Pilarczyk, D. Przyczyna, M. Suchecki, P. Zawal, K. Szaciłowski, Heavy pnictogen

chalcohalides: the synthesis, structure and properties of these rediscovered semiconductors, Chem. Commun. 54 (2018) 12133–12162, https://doi.org/10.1039/c8cc05149f.

- [22] M. Huang, Z. Zheng, Z. Dai, X. Guo, S. Wang, L. Jiang, J. Wei, S. Chen, DASP: defect and dopant ab-initio simulation package, J. Semiconduct. 43 (2022), https://doi. org/10.1088/1674-4926/43/4/042101.
- [23] Z.S. Aliev, S.S. Musaeva, D.M. Babanly, A.V. Shevelkov, M.B. Babanly, Phase diagram of the Sb-Se-I system and thermodynamic properties of SbSeI, J. Alloys Compd. 505 (2010) 450–455, https://doi.org/10.1016/j.jallcom.2010.06.103.
- M. Nowak, Photoferroelectric Nanowires, 2010, https://doi.org/10.5772/39496.
 S. Jeon, G. Cho, W. Kim, S.-I. Kwun, Optical properties of SbSi: Co and SbSel: Co
- single crystals, Solid State Commun. 68 (1988) 1043–1046, https://doi.org/ 10.1016/0038-1098(88)90422-X.
- [26] S.K. Balakrishnan, P.C. Parambil, E. Edri, Mechanistic insight into the topotactic transformation of trichalcogenides to chalcohalides, Chem. Mater. 34 (2022) 3468–3478, https://doi.org/10.1021/acs.chemmater.2c00306.
- [27] F. Palazon, Metal chalcohalides: next generation photovoltaic materials? Sol. RRL 6 (2022) https://doi.org/10.1002/solr.202100829, 1–9.
- [28] Y. Zhou, L. Wang, S. Chen, S. Qin, X. Liu, J. Chen, D.J. Xue, M. Luo, Y. Cao, Y. Cheng, E.H. Sargent, J. Tang, Thin-film Sb₂Se₃ photovoltaics with oriented onedimensional ribbons and benign grain boundaries, Nat. Photonics 9 (2015) 409–415, https://doi.org/10.1038/nphoton.2015.78.
- [29] Y. Di Luo, R. Tang, S. Chen, J.G. Hu, Y.K. Liu, Y.F. Li, X.S. Liu, Z.H. Zheng, Z.H. Su, X.F. Ma, P. Fan, X.H. Zhang, H.L. Ma, Z.G. Chen, G.X. Liang, An effective combination reaction involved with sputtered and selenized Sb precursors for efficient Sb₂Se₃ thin film solar cells, Chem. Eng. J. 393 (2020) 124599, https://doi. org/10.1016/j.cej.2020.124599.
- [30] M. Grossberg, O. Volobujeva, A. Penežko, R. Kaupmees, T. Raadik, J. Krustok, Origin of photoluminescence from antimony selenide, J. Alloys Compd. 817 (2020) 1–5, https://doi.org/10.1016/j.jallcom.2019.152716.
- [31] S. Li, H. Shen, J. Chen, Y. Jiang, L. Sun, A. Raza, Y. Xu, Effect of selenization temperature on the properties of Sb₂Se₃ thin films and solar cells by two-step method, J. Mater. Sci. Mater. Electron. 30 (2019) 19871–19879, https://doi.org/ 10.1007/s10854-019-02354-1.
- [32] A. Shongalova, M.R. Correia, B. Vermang, J.M.V. Cunha, P.M.P. Salomé, P. A. Fernandes, On the identification of Sb₂Se₃ using Raman scattering, MRS Commun 8 (2018) 865–870, https://doi.org/10.1557/mrc.2018.94.
- [33] A. Kumar, V. Kumar, A. Romeo, C. Wiemer, G. Mariotto, Raman spectroscopy and in situ XRD probing of the thermal decomposition of Sb₂Se₃ thin films, J. Phys. Chem. C 125 (2021) 19858–19865, https://doi.org/10.1021/acs.jpcc.1c05047.
- [34] G. Lucovsky, A. Mooradian, W. Taylor, G.B. Wright, R.C. Keezer, Identification of the fundamental vibrational modes of trigonal, α - monoclinic and amorphous selenium, Solid State Commun. 5 (1967) 113–117, https://doi.org/10.1016/0038-1098(67)90006-3.
- [35] S.K. Balakrishnan, P.C. Parambil, L. Houben, M. Asher, O. Yaffe, E. Edri, Revealing hidden phases and self-healing in antimony trichalcogenides and chalcoiodides, Cell Reports Phys. Sci. 4 (2023) 101298, https://doi.org/10.1016/j. xcrp.2023.101298.
- [36] G. Kanchana, D. Arivuoli, Spectroscopic investigation of BiSeI, SbSeI compounds and BiSbS_xSe_{1-x}I solid solutions, Indian J. Eng. Mater. Sci. 8 (2001) 373–376.
- [37] R. Bai, B. Xiao, F. Li, X. Liu, S. Xi, M. Zhu, W. Jie, B. Bin Zhang, Y. Xu, Growth of bismuth- and antimony-based chalcohalide single crystals by the physical vapor transport method, CrystEngComm 24 (2022) 1094–1099, https://doi.org/ 10.1039/d1ce01602d.
- [38] A. Escobedo Morales, E. Sánchez Mora, U. Pal, Use of diffuse reflectance spectroscopy for optical characterization of un-supported nanostructures, Rev. Mexic. Fisica S. 53 (2007) 18–22. https://www.redalyc.org/articulo.oa?id=57 028299004.
- [39] G.D. Gesesse, A. Gomis-Berenguer, M.F. Barthe, C.O. Ania, On the analysis of diffuse reflectance measurements to estimate the optical properties of amorphous porous carbons and semiconductor/carbon catalysts, J. Photochem. Photobiol. Chem. 398 (2020), https://doi.org/10.1016/j.jphotochem.2020.112622.
- [40] A.C. Wibowo, C.D. Malliakas, Z. Liu, J.A. Peters, M. Sebastian, D.Y. Chung, B. W. Wessels, M.G. Kanatzidis, Photoconductivity in the chalcohalide semiconductor, SbSeI: a new candidate for hard radiation detection, Inorg. Chem. 52 (2013) 7045–7050, https://doi.org/10.1021/ic401086r.
- [41] T. Schmidt, K. Lischka, W. Zulehner, Excitation-power dependence of the nearband-edge photoluminescence of semiconductors, Phys. Rev. B 45 (1992) 8989–8994, https://doi.org/10.1103/PhysRevB.45.8989.
- [42] J. Krustok, H. Collan, K. Hjelt, Does the low-temperature Arrhenius plot of the photoluminescence intensity in CdTe point towards an erroneous activation energy? J. Appl. Phys. 81 (1997) 1442–1445, https://doi.org/10.1063/1.363903.
- [43] J. Krustok, J. Raudoja, J.H. Schön, M. Yakushev, H. Collan, Role of deep donordeep acceptor complexes in CIS-related compounds, Thin Solid Films 361 (2000) 406–410, https://doi.org/10.1016/S0040-6090(99)00756-7.
- [44] J. Krustok, H. Collan, K. Hjelt, J. Mädasson, V. Valdna, Photoluminescence from deep acceptor-deep donor complexes in CdTe, J. Lumin. 72–74 (1997) 103–105, https://doi.org/10.1016/S0022-2313(97)00061-6.
- [45] F. Williams, Donor—acceptor pairs in semiconductors, Phys. Status Solidi. 25 (1968) 493–512, https://doi.org/10.1002/pssb.19680250202.
- [46] J. Krustok, T. Raadik, M. Grossberg, M. Kauk-Kuusik, V. Trifiletti, S. Binetti, Photoluminescence study of deep donor- deep acceptor pairs in Cu₂ZnSnS₄, Mater. Sci. Semicond. Process. 80 (2018) 52–55, https://doi.org/10.1016/j. mssp.2018.02.025.