

DOCTORAL THESIS

Development of Bi_2S_3 -Based
Materials by Close-Spaced
Sublimation for Thin-Film
Solar Cell Applications

Mykhailo Koltsov

TALLINN UNIVERSITY OF TECHNOLOGY
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Development of Bi_2S_3 -Based Materials by Close-Spaced Sublimation for Thin- Film Solar Cell Applications

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Declaration:

Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Mykhailo Koltsov

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**Bi₂S₃-põhiste materjalide väljatöötamine
lähidistants-sublimatsiooni meetodil
kasutamiseks õhukesekilelistes
päikesepatareides**

MYKHAILO KOLTSOV

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List of publications

The present Ph.D. thesis is based on the following publications that are referred to in the text by Roman numbers.

- I. **M. Koltsov**, S.V. Gopi, T. Raadik, J. Krustok, R. Josepson, R. Gržibovskis, A. Vembris, and N. Spalatu, "Development of Bi_2S_3 thin film solar cells by close-spaced sublimation and analysis of absorber bulk defects via in-depth photoluminescence analysis", *Solar Energy Materials and Solar Cells*, 254, 112292, 2023, DOI: 10.1016/j.solmat.2023.112292.
- II. **M.A. Koltsov**, G. Colibaba, D. Miliaieva, E. Dudutienė, M. Guc, V. Rotaru, D. Untila, J. Hiie, M. Krunks, I. Oja Acik, and N. Spalatu, "Composition-tunable $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution thin films via close-spaced sublimation", *Journal of Alloys and Compounds*, 1065, 188010, 2026, DOI: 10.1016/j.jallcom.2026.188010.
- III. **M.A. Koltsov**, R. Schwiddessen, D. Abou-Ras, S. Schorr, I. Oja Acik, and N. Spalatu, "Understanding the correlation between deposition conditions and nanoribbon orientation in close-spaced sublimated $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin film solid solutions", *Journal of Alloys and Compounds*, 1073, 189037, 2026, DOI: 10.1016/j.jallcom.2026.189037.

Author's contribution to the publications

- I. Deposition of Bi_2S_3 thin films by close-spaced sublimation (CSS); material characterization by X-ray diffraction (XRD), UV-Vis spectroscopy, Raman spectroscopy, and Van der Pauw measurements; device characterization by J-V curve analysis and external quantum efficiency (EQE); data analysis and visualization; major role in writing.
- II. Synthesis of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions; deposition of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films by CSS; material characterization by XRD, Raman spectroscopy, UV-Vis, and Van der Pauw measurements; device characterization by J-V curve analysis and EQE; data analysis and visualization; major role in writing.
- III. Deposition of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films by CSS; material characterization by X-ray fluorescence (XRF), Bragg-Brentano XRD (BBXRD), texture-XRD, and grazing-incidence XRD (GIXRD); data analysis and visualization; major role in writing.

Introduction

The global transition toward distributed and renewable energy sources has placed photovoltaics (PV) at the center of electricity generation strategies, with installed solar capacity surpassing 2 TW in 2024 and projected to reach 5 TW by 2030 [1,2]. Crystalline silicon (c-Si) dominates the market but requires energy-intensive processing; thin-film technologies based on CdTe and Cu(In,Ga)Se₂ (CIGS) are less material- and energy-expensive during solar cell production, but their reliance on toxic (Cd) or scarce (Te, In, Ga) elements limits scalability [3–5]. This has motivated the search for thin-film absorbers composed of earth-abundant, non-toxic elements with suitable optoelectronic properties for solar energy conversion [6].

Quasi-one-dimensional (Q1D) antimony and bismuth chalcogenides – Sb₂S₃, Sb₂Se₃, Bi₂S₃, and their solid solutions (Sb_xBi_{1-x})₂(S_ySe_{1-y})₃ – are a class of emerging absorber materials for thin-film photovoltaic (PV) devices, with earth-abundant, non-toxic constituents and bandgaps suitable for solar energy conversion [7]. Q1D chalcogenide materials crystallize in the orthorhombic structure as [C₄A₆]_n nanoribbons; covalent bonding holds atoms within each nanoribbon, while weaker van der Waals forces keep the nanoribbons together [8]. Grain boundaries in these materials are free of dangling bonds, and carrier transport is strongly anisotropic along the ribbon axis [9,10]. The orientation of nanoribbons relative to the substrate is therefore a key parameter for efficient charge collection in thin-film solar cells.

Among the antimony-based members of this family, power conversion efficiencies (PCEs) of 8.36% for Sb₂S₃, 10.58% for Sb₂Se₃, and 11.02% for Sb₂(S_ySe_{1-y})₃ have been reported [11], and the field has been growing rapidly over the past decade. Physical vapor deposition techniques, particularly close-spaced sublimation (CSS) and vapor transport deposition (VTD), have been used to deposit Q1D chalcogenide thin films with controlled nanoribbon orientation [12,13].

In contrast, Bi₂S₃ – the bismuth-based member of the Q1D family – remained understudied despite sharing the orthorhombic crystal structure and offering the advantages of even lower toxicity and higher abundance compared with Sb-based members [10,14]. Very few studies on Bi₂S₃ solar cells were published, the vast majority employing chemical deposition techniques (CBD, hydrothermal, SILAR) to produce nanocrystalline absorbers; only two studies reported solar cells with physically deposited Bi₂S₃ absorbers – by thermal evaporation [15] and rapid thermal evaporation [16]. CSS deposition of Bi₂S₃ had not been attempted, despite the demonstrated success of CSS for the structurally analogous Sb₂Se₃ and Sb₂S₃. Even less research was published on the (Sb_xBi_{1-x})₂S₃ solid solution systems, with one study on solar cells [17] and one on physical thin-film deposition [18]. No systematic investigation of texture and nanoribbon orientation as a function of both composition and deposition conditions existed for this system.

The aim of this doctoral thesis, therefore, is to develop the CSS deposition protocols for Bi₂S₃ and (Sb_xBi_{1-x})₂S₃ thin films with different [Sb]:[Bi] ratios and to provide an understanding of the impact of CSS deposition conditions on the morphological, structural, and optoelectronic properties of the deposited films. Deposition protocols for the deposition of densely-packed, continuous thin films were provided for Bi₂S₃ and five different (Sb_xBi_{1-x})₂S₃ solid solutions (x = 0.1, 0.33, 0.5, 0.67, and 0.9). Bi₂S₃ thin films were

characterized by a low-temperature photoluminescence to learn more about the defect structure of this material. For all studied compositions, the chemical composition, optoelectronic properties, structure, and texture were characterized, with the latter being analyzed in-depth via complementary X-ray diffraction techniques and electron backscatter diffraction (EBSD). Proof-of-concept solar cell devices were fabricated and characterized, highlighting the viability of these materials as thin-film PV absorbers.

The thesis is structured as follows. Chapter 1 presents a literature review covering the PV context, Q1D chalcogenide absorber materials, thin-film deposition techniques with a focus on CSS, texture characterization methodology, and the current state of research on Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$. Chapter 2 describes the experimental methodology, including solid solution synthesis, CSS thin-film deposition, the set of thin-film characterization techniques employed (SEM/EDX, XRF, Hall measurement, UV-Vis, PL, Raman, BBXRD, GIXRD, texture XRD, EBSD), and solar cell fabrication and characterization. Chapter 3 presents the results and discussion organized into three sections corresponding to the three publications: (3.1) CSS deposition and characterization of Bi_2S_3 thin films and solar cells, including defect analysis by low-temperature PL; (3.2) synthesis, CSS deposition, optoelectronic properties, and nanoribbon orientation of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions, along with a proof-of-concept solar cell device; and (3.3) in-depth texture and structural characterization of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films by BBXRD, GIXRD, texture XRD, and EBSD. The thesis concludes with a summary of the main findings.

Abbreviations

a-Si	Amorphous silicon
ALD	Atomic layer deposition
BBXRD	Bragg-Brentano XRD
c-Si	Crystalline silicon
CBD	Chemical bath deposition
CBM	Conduction band minimum
CIGS	Copper Indium Gallium Selenide
CSS	Close-spaced sublimation
CVD	Chemical vapor deposition
CZTS	Copper Zinc Tin Sulfide
DAP	Donor–acceptor pair
DD-DA	Deep Donor - Deep Acceptor
DFT	Density functional theory
DSSC	Dye-sensitized solar cells
EBS	Electron Backscatter Diffraction
EDX	Energy-dispersive X-ray spectroscopy
E _g	Bandgap energy
EIS	Electrochemical impedance spectroscopy
EQE	External quantum efficiency
ER-EIS	Energy-resolved electrochemical impedance spectroscopy
ETL	Electron transport layer
FF	Fill factor
FTO	Fluorine-doped tin oxide
FWHM	Full width at half maximum
GIXRD	Grazing-incidence XRD
ICDD	International Centre for Diffraction Data
ICSD	Inorganic Crystal Structure Database
IPF	Inverse pole figure
ITO	Indium tin oxide
J-V	Current density – voltage characterization
JCPDS	Joint Committee on Powder Diffraction Standards
J _{sc}	Short-circuit current density
LED	Light-emitting diode
MOCVD	Metal-organic chemical vapor deposition
NIR	Near-infrared
OGR	Optimal growth regime
PCE	Power conversion efficiency
PF	Pole figure
PL	Photoluminescence
PV	Photovoltaics
PVD	Physical vapor deposition
Q1D	Quasi-one-dimensional

QD	Quantum dots
RCT	Ribbon carrier transport
RF	Radiofrequency
RT	Room temperature
RTE	Rapid thermal evaporation
SCR	Space charge region
SEM	Scanning electron microscopy
SILAR	Successive ionic layer adsorption and reaction
SLME	Spectroscopic limited maximum efficiency
TC	Texture coefficient
TE	Thermal evaporation
TEC	Thermal expansion coefficient
T _{so}	Source temperature
T _{sub}	Substrate temperature
USP	Ultrasonic spray pyrolysis
UV	Ultraviolet
UV-Vis	Ultraviolet-visible spectroscopy
VBM	Valence band maximum
V _{oc}	Open-circuit voltage
VTD	Vapor transport deposition
XRD	X-ray diffraction
XRF	X-ray fluorescence
α'	Nanoribbon tilt angle from substrate normal

1 Literature review

In this chapter, the general photovoltaic context of the current research and its direct background in chalcogenide photovoltaic (PV) are provided. Emerging chalcogenide PV technologies are described in more detail, with a special focus on quasi-1D (Q1D) materials and, ultimately, Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, including the development of Bi_2S_3 solar cells and associated defect studies. The commonly used thin-film deposition techniques employed in thin-film solar cell manufacturing are described, with special attention to the physical techniques and close-spaced sublimation (CSS). The chapter concludes with a summary of the identified gaps and the aims of the thesis.

1.1. Photovoltaics – brief history and fundamentals

The key principle, lying at the basis of all solar cells, from first experiments to the modern state-of-the-art devices, is the photovoltaic effect - the generation of a potential difference at the junction of two different materials (usually p-type and n-type semiconductors) in response to electromagnetic radiation [19]. It can be divided into three subprocesses:

1. Generation of charge carriers due to the absorption of photons in the materials that form a junction via excitation of electrons, which leave behind holes;
2. Subsequent separation of the photo-generated charge carriers in the junction, which prevents radiative and non-radiative recombination losses;
3. Collection of the photo-generated charge carriers at the terminals of the junction, where chemical energy of electron-hole pairs converts to electric energy [19].

This concept was first discovered in 1839 by Alexandre Edmond Becquerel as "the production of an electric current when two plates of platinum or gold immersed in an acid, neutral, or alkaline solution are exposed in an uneven way to solar radiation" [20]. Thirty-four years later, in 1873, Willoughby Smith discovered the photovoltaic effect in selenium [21] – and the first selenium solar cell was built in 1883 by Charles Fritts [22]. The first comprehensive theoretical work regarding the photovoltaic effect was by Albert Einstein (1905, Nobel Prize in 1921) [23]. For the next half-century, both experimental and theoretical works in the fields of electricity and crystal growth were agglomerating. Then, on April 25, 1954, Bell Labs announced the first practical silicon solar cell with a power conversion efficiency (PCE) of 6% - so the era of solar energy as a field of energetics, not just science, began [24]. Starting from the high-end markets, such as military and space applications (e.g., the Vanguard-1 satellite in 1958), PV energy sources demonstrated their viability in harsh environments and remote locations [25]. The oil crisis of 1973 catalyzed a market expansion of governmentally supported PV manufacturing and research in the US, shifting from niche applications to a prospective large-scale energy source [26,27]. Partially, this R&D impulse stimulated the development of the first thin-film photovoltaic technologies as alternatives to silicon, such as CdTe [28–31] and chalcopyrites or CIGS [32–34]. These technologies accompanied silicon-based solar cells on the actively growing PV market [2]. Other technologies, such as gallium arsenide solar cells [35–38] (efficient, but expensive, suitable for the high-end market), dye-sensitized solar cells [39,40], organic solar cells

[41–44], quantum dot solar cells [45–48], solar cells on the basis of perovskites [49–51], kesterites [3,52–54], and emerging chalcogenide materials [4,5] followed during the next decades (Figure 1).

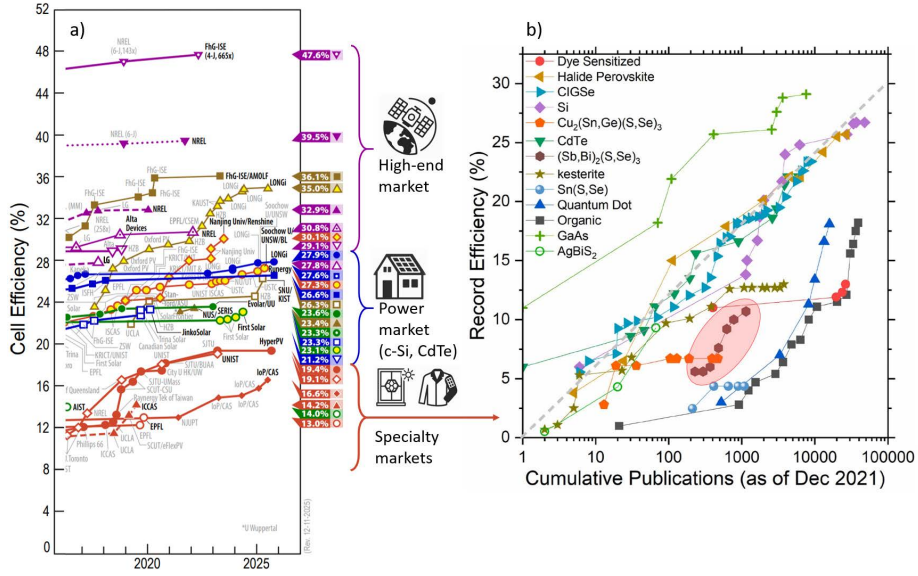


Figure 1. The current state of the photovoltaic research (a) as a function of time (excerpt from the NREL diagram) [55] and (b) as a function of effort (in cumulative number of publications) [56].

Crystalline silicon (c-Si) based single-junction solar cells are currently dominating the terrestrial solar power market due to their high efficiency (above 20%), low cost (below 0.5\$/W), and high reliability (~25 years). The first generation of thin-film technologies, such as CdTe and Cu(In,Ga)Se₂ (CIGS), have reached comparable efficiency to c-Si and have become industrially established, while requiring ~100 times thinner absorber material and less energy to be used in the manufacturing process compared to Si (≥ 100 μm) [34]. Hybrid organic-inorganic perovskite CH₃NH₃PbI₃ (MAPI) solar cells, whose single-junction efficiencies rapidly reached ~25%, offered a timely demonstration of the potential of emerging materials to address (though still with some stability issues) the long-standing bottleneck to cost-effective scale-up and commercialization [50]. The emergence of new PV applications (such as building-integrated PV, product-integrated PV, and the internet of things) would require diversifying the portfolio of existing PV technologies by adopting new solar cell designs and emerging materials to implement cost-effective, low-impact solutions. At this scale, for a new PV technology, it is insufficient to be only competitive with current technologies in efficiency and reliability; it should also be green, environmentally friendly, and comprise earth-abundant chemical elements [4,5].

An emerging class of highly promising PV materials, currently under widespread investigation in the PV community, is inorganic chalcogenide compounds based on non-cubic semiconductors such as Sb₂Se₃, Sb₂S₃, Bi₂S₃, and their related alloys/solid solutions

(generalizable as $(\text{Sb}_x\text{Bi}_{1-x})_2(\text{S}_y\text{Se}_{1-y})_3$) [7,56], as well as other related materials - Cu_3SbS_3 , CuSbS_2 , CuBiS_2 , Cu_2SnS_3 , etc.

There are several noticeable features that make these emerging inorganic materials scientifically interesting and distinct from traditional thin-film technologies – the consistency of the abundant and non-toxic elements [6], high absorption with a tailorable bandgap (especially for the solid solutions), defect tolerance [57], flexible device architectures [58–61], and the implementability of the knowledge, previously gained for the CdTe and CIGS technologies.

1.2. Sb- and Bi-based chalcogenide PV materials

$(\text{Sb}_x\text{Bi}_{1-x})_2(\text{S}_y\text{Se}_{1-y})_3$ group of materials, or antimony-bismuth chalcogenides, includes Sb_2Se_3 , Sb_2S_3 , Bi_2S_3 , Bi_2Se_3 , as well as their solid solutions (Figure 2a, Table 1). Sb, Bi, S, and Se are earth-abundant [62,63], low-cost materials which show far lower toxicity for both human beings and natural environments, compared with Cd, Te, In, Ga, and, especially, As [64,65] – which significantly contributed to the initial motivation for their development. All of them, with the exception of rhombohedral Bi_2Se_3 , are single-phase [66] orthorhombic (space group 62) quasi-one-dimensional (Q1D) materials, usually interpreted in terms of $Pnma$ or $Pbnm$ space groups (Table 1, Figure 2b), out of which the ***Pnma* notation is to be used as standard throughout this work.**

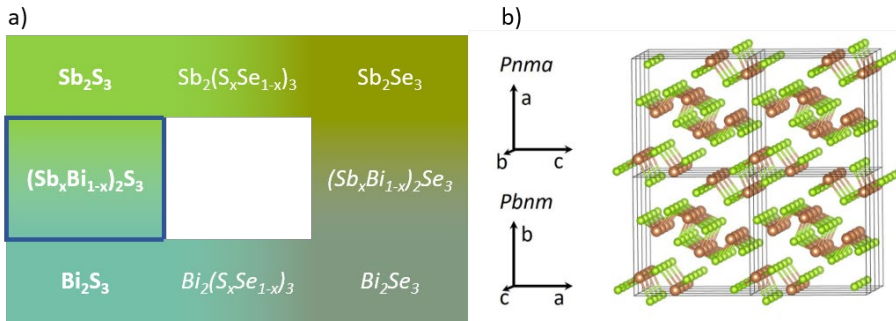


Figure 2 (from Publication III). (a) $(\text{Sb}_x\text{Bi}_{1-x})_2(\text{S}_y\text{Se}_{1-y})_3$ materials with the highlighted $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ as a solid solution of interest. Materials with non-orthorhombic phases (based on Bi_2Se_3) are given in italic. (b) Two indexing conventions for orthorhombic unit cells of $(\text{Sb}_x\text{Bi}_{1-x})_2(\text{S}_y\text{Se}_{1-y})_3$. In the first convention, $Pnma$, ribbons lie parallel to the b -axis, while in the second convention, $Pbnm$, ribbons lie parallel to the c -axis. Cation atoms (Sb or Bi) are given in brown, anion atoms (S or Se) are given in green. [67]

Instead of the formation of three-dimensional crystal structures, like Si, CdTe, and GaAs, Q1D materials (such as $(\text{Sb}_x\text{Bi}_{1-x})_2(\text{S}_y\text{Se}_{1-y})_3$) form nanoribbons [7]. Covalent bonding keeps the atoms together within the nanoribbon, while weaker van der Waals bonding keeps these nanoribbons together [8]. The Q1D structure means that no lattice breaking is required for termination at grain boundaries in Bi-chalcogenides, making the grain boundaries in such materials "defect-tolerant" or "having benign grain boundaries" [7,9,10,57,68].

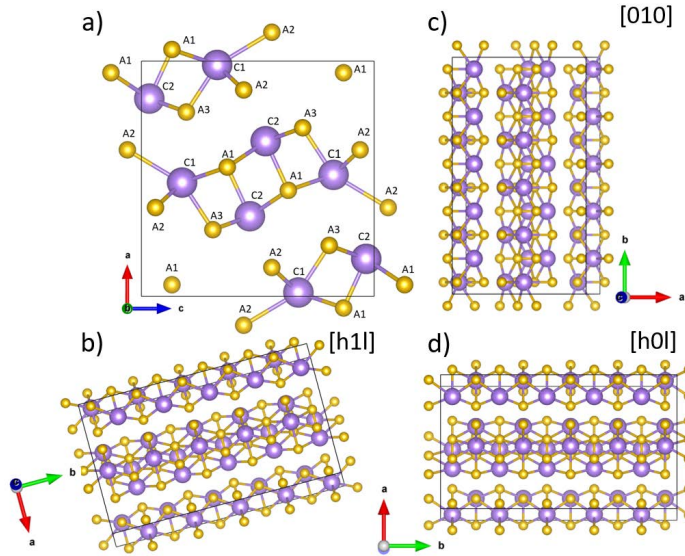


Figure 3. Schematic diagram of $(Sb_xBi_{1-x})_2(S_ySe_{1-y})_3$ orthorhombic unit cell and crystallographic orientations b) [h1l], c) [010], and d) [h0l] in *Pnma* notation. Cation atoms (C, meaning Sb or Bi) are given in violet, anion atoms (A, meaning S or Se) are given in yellow [12,66,69].

In antimony-bismuth chalcogenides, such a crystal structure is composed of $[C_4A_6]_n$ nanoribbons, which include two cation sites (C1, C2), occupied by Sb or Bi, and three anion sites (A1, A2, and A3), occupied by S or Se (Figure 3) [66,70–72].

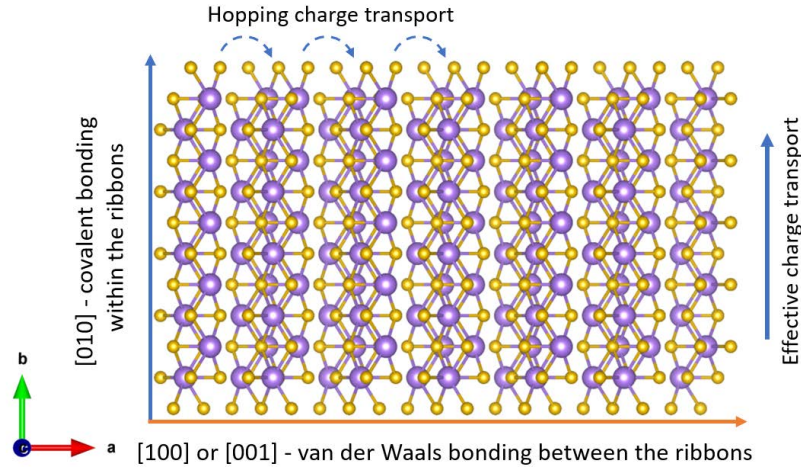


Figure 4. Anisotropic carrier transport along and between the ribbons of 1D orthorhombic $(Sb_xBi_{1-x})_2(S_ySe_{1-y})_3$ material. Reproduced from [73] with conversion to *Pnma* notation.

In *Pnma* notation, these nanoribbons are oriented along the [010] crystal direction or *b*-axis, with the strong covalent C-A bonding within the chain [72,74]. At the same time, the neighboring nanoribbons are held together by weak van der Waals forces in [100]

and [001] directions. Such differences in bonding mechanisms result in anisotropic mechanical [75] and optoelectronic properties, high absorption coefficients, and chemical stability [13]. In particular, carrier transport along the $[C_4A_6]_n$ ribbons is considerably more favorable than between them (Figure 4). For low-dimensional materials, the surface energy of the crystalline plane, parallel to the van der Waals force, is always lower than the surface energy of the crystalline plane, parallel to the direction of covalent bonding [76]. According to the principle of minimum energy, nanoribbons of Q1D materials tend to grow parallel to the substrate, minimizing surface energy and impeding the nanoribbon growth in other directions, especially perpendicular to the substrate [77]. Decreased dimensionality facilitates charge transport along nanoribbons or sheets and impedes it between them, making the nanoribbon/sheet growth direction (generally regarded as **texture**) crucial for the performance of thin-film PV devices [12,78–80].

The main properties of $(Sb_xBi_{1-x})_2(S_ySe_{1-y})_3$ binary chalcogenides are given in Table 1. As shown in Table 1, Sb_2S_3 , Sb_2Se_3 , and Bi_2S_3 are isomorphic materials [81,82], which share the same orthorhombic crystal structure with the $Pnma$ space group and similar lattice parameters. At the same time, their optoelectronic properties differ considerably, leading to differences in solar cell performance. For example, the wider bandgap of Sb_2S_3 leads to significantly higher V_{oc} in solar cells, compared with Sb_2Se_3 , while having lower J_{sc} values [83].

Table 1. $(Sb_xBi_{1-x})_2(S_ySe_{1-y})_3$ binary chalcogenides – main material properties.

	Melting point	Crystal structure	a, b, c lattice parameters, Å	Bandgap, eV	Prevailing conductivity type	Resistivity, Ohm*cm	Record solar cell PCE to date, %	Refs
Sb_2Se_3	612°C	orthorhombic, $Pnma$ or $Pbnm$	11.79, 3.98, 11.67	1.1-1.3	p	10^6	10.58%	[12,84–86]
Sb_2S_3	546°C	orthorhombic, $Pnma$ or $Pbnm$	11.23, 3.75, 11.31	1.7-1.8	p	10^{6-8}	8.36%	[87–91]
Bi_2S_3	775°C	orthorhombic, $Pnma$ or $Pbnm$	11.26, 3.95, 11.12	0.9-1.36 (indirect) 1.3-1.7 (direct)	n	10	3.3%	[92]
Bi_2Se_3	710°C	rhombohedral, $R\bar{3}mH$ or $R\bar{3}mR$	4.14, 4.14, 28.66, $\gamma=120^\circ$	0.35-0.6	n	10^{-5}	0.28%	[93,94]

Synthesis of the $Sb_2(S_ySe_{1-y})_3$ solid solution [95] with a particular $[S]:[Se]$ ratio provides an opportunity to tune the bandgap in the range of 1.1 eV (Sb_2Se_3) to 1.8 eV (Sb_2S_3) and to reduce the defect-induced recombination losses, making it more suitable for both single-junction and multijunction solar cells [96]. In this way, the research in both Sb_2S_3 and Sb_2Se_3 binary compounds provided a natural foothold for the quasi-binary $Sb_2(S_ySe_{1-y})_3$. Both physical deposition techniques, such as TE [97] and VTD [98], and chemical deposition techniques, such as sequential CBD [99] and hydrothermal deposition [100], are actively used in $Sb_2(S_ySe_{1-y})_3$ research, with the latter being used in the deposition of the champion solar cells with the record PCE of 11.02% [101].

Quasi-binary systems, which involve Bi_2Se_3 as one of their end members, namely $(\text{Sb}_x\text{Bi}_{1-x})_2\text{Se}_3$ and $\text{Bi}_2(\text{S}_y\text{Se}_{1-y})_3$, are less researched in the PV context, given the phase transition between the orthorhombic and rhombohedral [102]. $(\text{Sb}_x\text{Bi}_{1-x})_2\text{Se}_3$ potential as an absorber for narrow-bandgap devices was recognized, but has rarely been studied [94]. $(\text{Sb}_x\text{Bi}_{1-x})_2\text{Se}_3$ thin films, grown by co-evaporation with the subsequent annealing, were applied as thin-film PV absorbers in combination with CdS/ZnO electron transport layers (ETLs) to get the PV devices with the highest PCE of 0.7% for $(\text{Sb}_{0.569}\text{Bi}_{0.431})_2\text{Se}_3$ [103]. The presence of the aforementioned phase transition and the narrowness of the Bi_2Se_3 bandgap (0.35-0.6 eV) are among the factors that have limited further research in this area.

Further insights into the Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems are given in Sections 1.3. and 1.4, respectively.

1.3. Development of Bi_2S_3 functional coatings and solar cells

Bismuth is widely regarded as non-toxic, chemically stable, and already used in consumer and medical products (such as Pepto-Bismol) – an important advantage for scalable, environmentally safe PV technologies [14]. As well as antimony, bismuth is an abundant metal in the Earth's crust [104,105,4]; it is a byproduct of Pb, Cu, and Sn refining and has significant commercial applications, resulting in a relatively low and stable price [3,64]. Nevertheless, Bi_2S_3 and Bi_2Se_3 are far less studied than Sb-based materials, despite their many similarities.

Beyond photovoltaics, Bi_2S_3 has attracted considerable research interest across numerous applications, reflecting its versatile optoelectronic, catalytic, and physicochemical properties [106,107]. In thermoelectrics, the structural anisotropy and tellurium-free composition of Bi_2S_3 make it an attractive n-type thermoelectric material [108,109]. Bi_2S_3 nanostructures have demonstrated high photoresponsivity in visible-to-NIR photodetectors [110] and sensitivity in X-ray detection for medical applications [111,112]. As a catalyst, Bi_2S_3 has been employed for photoelectrochemical water oxidation [113] and CO_2 photoreduction [114], while Bi_2S_3 -derived nanosheets exhibited notable electrocatalytic activity for CO_2 reduction to formate [115,116]. In energy storage, Bi_2S_3 serves as a high-capacity anode material for sodium-ion [117] and potassium-ion batteries [118].

In thin-film photovoltaics, Bi_2S_3 is less researched than Sb_2S_3 and Sb_2Se_3 , despite a number of distinct advantages, such as a high absorption coefficient (10^5 cm^{-1}), and absorption onset in the infrared region [10], exhibiting both n-type [119] and p-type [120] conductivity [9,10].

While the conductivity type of Bi_2S_3 thin films has been widely reported, quantitative transport parameters (carrier concentration, mobility, and resistivity) have been systematically characterized primarily on single crystals. Hall effect measurements on Bridgman- and zone-melted crystals span n from $\sim 10^{15}$ to $\sim 10^{18} \text{ cm}^{-3}$ and μ from 5 to $350 \text{ cm}^2/\text{Vs}$ [121–124], with the wide spread attributed to sulfur stoichiometry – more stoichiometric crystals carrying fewer sulfur vacancy (V_S) donors and consequently higher mobility [123]. For thin films, resistivity ranges from $\sim 1 \Omega\cdot\text{cm}$ for well-crystallized spray pyrolysis films [125] to $\sim 10^4 \Omega\cdot\text{cm}$ for poorly crystalline chemically deposited films [126], while Hall mobility data were scarcer, for a solution-processed film reaching $\sim 7 \text{ cm}^2/\text{Vs}$

[127]. For stoichiometric Bi_2S_3 thin films deposited by physical techniques – thermal evaporation, reactive evaporation, and close-spaced sublimation – Hall-effect characterization had not been reported prior to the present work.

Both indirect and direct bandgaps were reported as possible for Bi_2S_3 in the range of 1.03–1.36 eV for indirect and 1.38–1.86 eV for direct bandgap [128–135,120,9,10,136]. Several studies have explored chemical solution-based deposition techniques, such as spin-coating [136], chemical bath deposition (CBD) [129], chemical vapor deposition (CVD) [137], metal-organic CVD (MOCVD) [138], ALD [120] and successive ionic layer adsorption and reaction (SILAR) [139]. In PV, chemical deposition techniques were mainly employed for Bi_2S_3 and the derived materials – Bi_2S_3 active layer inorganic/inorganic bulk heterojunction solar cells (with Bi_2S_3 nanowires) [92], colloidal Bi_2S_3 nanocrystals [140,141]. Solar cell devices with a PCE of 4.87% have been produced in the format of QD solar cells, with Bi_2S_3 nanocrystals blended with PbS QDs to form a bulk nano-heterojunction structure, which is the state of the art for such device architecture [141]. One significant drawback in all the above-mentioned Bi_2S_3 nanocrystal-based heterojunction structures is that nanocrystals are randomly oriented in the films. Therefore, some of them will be properly placed for conducting charges, while others will not, limiting charge transport and device PCE [10,138,139,141]. This limitation may be overcome by deposition techniques that can grow aligned nanoribbons, taking advantage of the natural anisotropic structure of Q1D materials – first and foremost, physical deposition techniques such as CSS, VTD, RTE, etc. However, few studies have focused on the physical deposition of Bi_2S_3 films for PV applications.

By 2022, the literature on Bi_2S_3 thin films is limited to 20–25 publications, relatively equally covering chemical (CBD, CVD, ALD, Spin-coating, etc.) and physical deposition techniques (TE, RTE, PVD, etc.) [120,129–134,142–147,15,16,148–153]. At least ten studies on Bi_2S_3 solar cells (mainly in DSSC and quantum dots) have been published, while just two publications [15,16] were focused on the physically deposited Bi_2S_3 as a solar cell absorber. Such a scale of the research, especially compared with the $\text{Sb}_2(\text{S,Se})_3$ area [85], indicates a vastly understudied field.

The first physical deposition of Bi_2S_3 was reportedly conducted in 1984 by Krishna Moorthy [142,154], including the deposition by the hot wall method – the physical deposition technique, from which later CSS was developed. For the first time, the morphological and chemical homogeneity of the CSS-deposited films was shown. In 1997–1998, Mahmoud et al. [129] and Rincón et al. [130] deposited Bi_2S_3 thin films by CBD and TE, comparing their bandgaps and finding both direct and indirect transitions. Later, dependence between the TE deposition conditions (namely, substrate temperature) and the crystalline and optoelectronic properties of the material was investigated by a few groups [131,133] while similar work for co-evaporation was conducted by Mesa et al. [134].

The first PV-related work in the field of physically deposited Bi_2S_3 was conducted by Haaf et al. [132], who varied the substrate temperature during the PVD deposition of Bi_2S_3 from 80 °C to 290 °C. Using confocal photoluminescence, the authors demonstrated the advantages of high-temperature deposition for optical properties (Table 2).

Table 2. Bi_2S_3 -based solar cell studies

Physical or chemical	Bi_2S_3 deposition technique	Bi_2S_3 form	Solar cell structure	PCE, %	Ref.
Chemical	Solventless thermolysis	Nanowires	ITO/PEDOT:PSS/MDMO-PPV: Bi_2S_3 /Al	0.0024%	[155]
	Sequential chemical deposition	Thin film	FTO/(X,A) Bi_2S_3 /PbS(A,B)/C/Ag	1%	[145]
	Solution processing	Nanocrystals	ITO/PbS QDs/ Bi_2S_3 NCs/Ag	1-1.6%	[140]
	Solution processing	Nanocrystals	ITO/Pb QDs/Pb+ Bi_2S_3 composite/ Bi_2S_3 NCs/Ag	4.87%	[141]
	Spin-coating	Nanocrystals	ITO/ Bi_2S_3 /P3HT/Ag	0.46%	[156]
	CBD	Thin film	TCO/ETL/ Bi_2S_3 /PbS (four ETLs tested)	0.1–0.4%	[146]
	Solvothermal synthesis	Nanowires	ITO/ TiO_2 /P3HT: Bi_2S_3 /MoO ₃ /Au	3.3%	[92]
Physical	SILAR	Quantum dots	FTO/c- TiO_2 /m- TiO_2 /s- TiO_2 / Bi_2S_3 /electrolyte/Cu ₂ S	1.63%	[157]
	TE	Thin film	Ag/n- Bi_2S_3 /p-Si/Al+Ag	0.24%	[15]
	TE	Thin film	ITO/p-NiO/n- Bi_2S_3 /Au	0.75%	[16]

As was mentioned, two works depicted solar cells with physically deposited Bi_2S_3 absorbers. Hasan [15] utilized the TE-deposited Bi_2S_3 as an absorber in Ag/n- Bi_2S_3 /p-Si/Al+Ag heterojunction devices, reaching up to a PCE of 0.24%. Song et al. [16] used RTE to produce a Bi_2S_3 absorber layer for ITO/p-NiO/n- Bi_2S_3 /Au solar cells, with source temperature around 600 °C and substrate temperatures between 100 °C and 300 °C, demonstrating a PCE of 0.75%.

As summarized in Table 2, Bi_2S_3 solar cell research has relied predominantly on chemically deposited nanocrystal-based device concepts, with the best-reported PCE of 4.87% [141], while physically deposited thin-film devices are limited to two studies with PCE below 1% [15,16]. Such a difference in achieved PCEs correlates with the amount of research and the corresponding lack of understanding in the relationship between the physical deposition conditions and the properties of the resulting thin-film solar cells.

1.3.1. Defect studies for Bi_2S_3

The number of available studies regarding the defect structure of Bi_2S_3 is also limited. A set of DFT-based studies was conducted [158,159], with the most thorough one (by Han et al.) providing the formation energies and ionization energy levels for various defects in Bi-rich and S-rich Bi_2S_3 (Figure 5), as well as exploring the effect of F, Cl, Br, I, Cu, Ag, and Pb dopings, with only Pb doping making it weakly p-type, while Cu, Cl, and Br were making Bi_2S_3 even stronger n-type semiconductor [159].

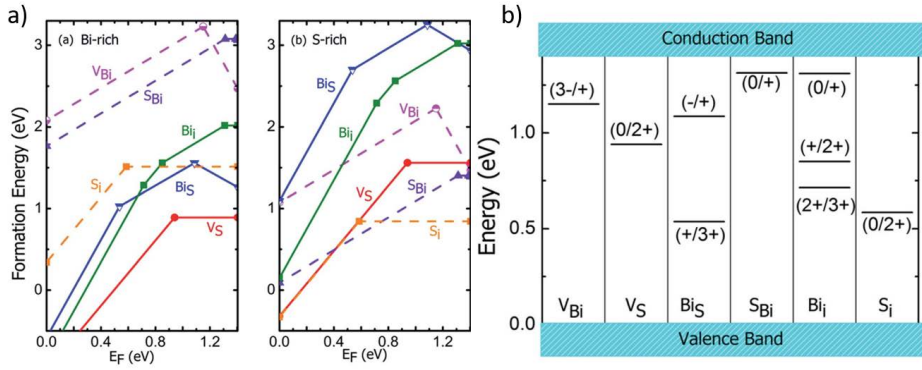


Figure 5. (a,b) Calculated formation energies of intrinsic defects as a function of Fermi levels under (a) Bi-rich, S-poor and (b) S-rich, Bi-poor conditions. The Fermi level is referenced to the valence band maximum (VBM) level, i.e., 0 is at the VBM level, and 1.4 eV (calculated bandgap) is at the conduction band minimum (CBM) level. (c) Calculated transition (ionization) energy levels of intrinsic point defects in the bandgap of Bi_2S_3 . Graphs are fully taken from [159].

Only vacancies of bismuth (V_{Bi}) and antisite (Bi_S) act as acceptor defects [159], but both these defects are deep (high) within the bandgap, close to the conduction band minimum, so that their ionization does not occur effectively in order to generate higher concentration hole carriers. The donor defects, such as vacancies of sulfur (V_S), were reported to have much lower formation energies for both Bi-rich/S-poor and Bi-poor/S-rich conditions, compared with acceptor-defects. Therefore, for Bi_2S_3 , n-type conductivity and higher electron concentration are usually expected. Most intrinsic point defects act as donors, including the interstitial sulfur defect (S_i), which is usually an acceptor in other chalcogenide semiconductors [160].

1.4. $(Sb_xBi_{1-x})_2S_3$ solid solutions

As reviewed in Sections 1.2 and 1.3, Sb_2S_3 and Bi_2S_3 are isomorphic orthorhombic materials that share a number of favorable properties for thin-film PV applications. From the perspective of physical deposition methods, both compounds have an additional practical advantage: their vapor pressures reach values sufficient for thin-film growth at source temperatures of 400–550 °C (Figure 6.a) [161,162], considerably lower than the temperatures typically required for established CSS-deposited absorbers such as CdTe (>600 °C) [163,164]. Furthermore, Sb_2S_3 and Bi_2S_3 are fully intersoluble, forming a continuous solid solution at all $[Sb]:[Bi]$ ratios (Figure 6.b), as established since 1919 [165,166]. This complete miscibility, combined with the accessibility of both end members to physical deposition techniques, makes the $(Sb_xBi_{1-x})_2S_3$ system an attractive candidate for composition-tunable thin-film absorbers.

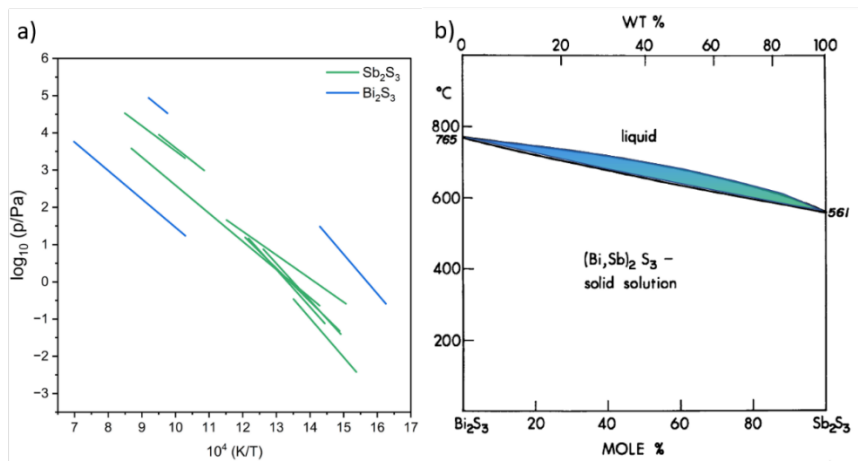


Figure 6. (a) Vapor pressures over Sb_2S_3 (green) and Bi_2S_3 (blue) according to the group of studies and assembled by Piacente et al [161,162]. (b) Summary of the phase relations in the condensed system Bi_2S_3 - Sb_2S_3 according to Springer and LaFlamme [166].

Compared with $\text{Sb}_2(\text{S}_y\text{Se}_{1-y})_3$ solid solutions, it has a few advantages:

- While $\text{Sb}_2(\text{S}_y\text{Se}_{1-y})_3$ solid solutions are the combinations of two p-type binary materials (Sb_2Se_3 and Sb_2S_3), $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ is a solid solution of p-type Sb_2S_3 and n-type Bi_2S_3 , which provides an opportunity for a broader range of applications [140,167,168].
- Similarly, the difference in resistivity between the Sb_2S_3 and Bi_2S_3 is 10^5 times larger than between Sb_2S_3 and Sb_2Se_3 , which provides an opportunity for a broader range of material properties.
- Finally, as it was given in Section 1.3, bismuth is less toxic compared with antimony [10,14], which may be a crucial metric, especially in the case of large-scale industrial applications.

However, the amount of research on $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ as a set of semiconductor materials is comparatively scarce, a few orders of magnitude scarcer than on $\text{Sb}_2(\text{S}_y\text{Se}_{1-y})_3$ [85], with only 22 studies related to $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ published up to 2024 (Figure 7, Table 3).

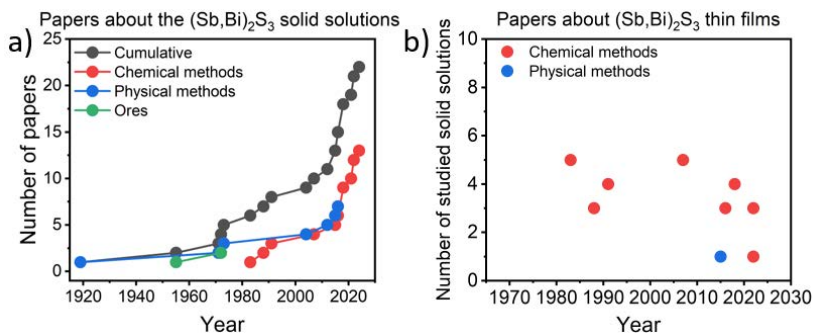


Figure 7 (From Publication II). (a) Current state of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution growth research, in particular (b) in the form of thin films.

The earliest studies of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ arose from mineralogical research on naturally occurring solid solutions found in Au-Ag-Cu ores [166,169]. Thermogravimetric characterization of various [Sb]:[Bi] ratios [170,171] established the near-linear dependence of melting points on composition. Among chemical deposition approaches, the remarkably thorough studies involving multiple [Sb]:[Bi] ratios were conducted using dip-dry-deposited thin films [172] and crystals grown by solventless thermolysis [173]. In terms of physical synthesis approaches, the most detailed study was conducted on high-temperature-synthesized single-crystal compositions, though not on thin films [167]. The available data show continuous, composition-dependent trends in optoelectronic and structural properties (Figures 8, 9), but coverage remains sparse and uneven across compositions, synthesis methods, and sample types.

Table 3. Most of the $(Sb_xBi_{1-x})_2S_3$ research available by 2026, besides the papers related to this thesis.

Type of synthesis	Year of publishing	Synthesis or deposition technique	Used term for $(Sb_xBi_{1-x})_2S_3$ systems	Approximate [Sb]:[Bi] ratios	Thin film	Solar cell	Ref.
Natural synthesis (mineralogy)	1955	-	Solid solution	11:9, 7:13	-	-	[169]
	1972	-	Solid solution	4:1, 3:2, 2:3, 1:4	-	-	[170]
Chemical	1983	Dip-Dry	Solid solution	6:1, 7:3, 3:2, 1:1, 3:7	+	-	[172]
	1988	Dip-Dry	Alloy	6:1, 1:1, 3:2	+	-	[174]
	1991	Solution pyrolysis	Solid solution	7:1, 5:2, 9:11, 3:5	+	-	[175]
	2007	Arrested precipitation	Ternary mixed chalcogenide	9:1, 4:1, 3:2, 2:3, 1:4	+	-	[176]
	2015	Hydrothermal	Solid solution	21:19	-	-	[177]
	2016	CBD	Doping	79:1, 39:1, 19:1	+	-	[178]
	2018	Solventless thermolysis	Solid solution	4:1, 3:2, 2:3, 1:4	-	-	[173]
	2018	Colloidal synthesis	Solid solution	7:1, 4:1, 3:2, 2:3, 1:4, 1:7	-	-	[179]
	2018	Cation exchange	-	4:1, 3:2, 2:3, 1:4	-	-	[180]
	2021	Cation exchange	Alloy	200:1	-	-	[181]
	2022	Hydrothermal	Doping	100:1, 50:1, 33:1	+	+	[17]
	2022	Cation exchange	Doping	Unclear	+	-	[182]
	2024	Hydrothermal	Alloy	Unclear	-	-	[183]
Physical	1919	High-temperature synthesis	Solid solution	9:1, 7:3, 3:7, 1:9	-	-	[165]
	1971	Solid-state synthesis	Solid solution	5:1, 4:1, 3:2, 1:1, 2:3, 1:4, 1:5	-	-	[166]
	1973	Solid-state synthesis	Solid solution	7:3, 1:1, 3:7	-	-	[184]
	2004	High-temperature synthesis	Solid solution	39:1, 33:7, 1:3, 9:11, 7:33, 3:17	-	-	[167]
	2012	Dry synthesis at low temperature	Solid solution	53:47	-	-	[185]
	2015	Thermal evaporation	Alloy	1:1 (S-deficient)	+	-	[18]

For physical vapor deposition, the sublimation behavior of the source material determines the deposition conditions and film stoichiometry. As shown in Figure 6.a, vapor pressures of the binary compounds were measured using the torsion-effusion and

Knudsen methods – for Sb_2S_3 in the 782–823K range [162] and for Bi_2S_3 in the 614–695K range [161,186]. These studies and prior mass spectrometric investigations [187] established that Sb_2S_3 mostly sublimes congruently, as $\text{Sb}_2\text{S}_3(\text{g})$, with $\text{SbS}(\text{g})$, $\text{S}_2(\text{g})$, and other species being minor contributors, while for Bi_2S_3 the decomposition to $\text{S}_2(\text{g})$ and $\text{BiS}(\text{g})$ is a dominant sublimation mechanism. These different sublimation mechanisms lead to vastly different vapor supersaturation at deposition conditions: low for Bi_2S_3 and several orders of magnitude higher for Sb_2S_3 . However, prior to the present work, such calculations had not been extended to the full $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution series, in which both Sb- and Bi-related vapor species coexist. How the dominant sublimation pathway transitions from the decomposition route in Bi-rich compositions to congruent sublimation in Sb-rich ones, and how this governs the CSS conditions for each $[\text{Sb}]:[\text{Bi}]$ ratio, remained unresolved.

The optical bandgaps of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ (Figure 8, Table 3) were characterized in a handful of studies by 2024: on spin-coated thin films with irregular $[\text{Sb}]:[\text{Bi}]$ ratios by Nomura et al [175], on a set of physically deposited and very S-rich (approx. $\text{Bi}_{0.9}\text{Sb}_{0.9}\text{S}_4$) thin films by Kandaswamy et al [18], on a set of chemically-synthesized films by Alqahtani et al [173], and three studies covered the deep doping of Sb_2S_3 by Bi_2S_3 by Shang et al [178], Mao et al [17] and Wang et al [182], all by chemical techniques (Figure 8). In two cases, in addition to the measured direct bandgaps, calculated indirect bandgaps were also provided [17,178].

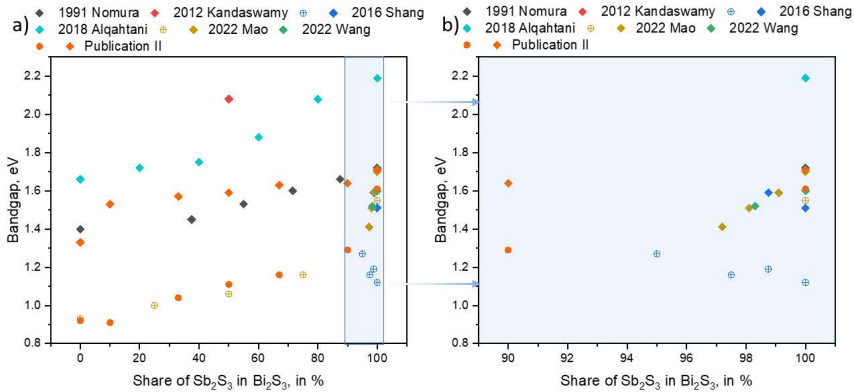


Figure 8. Direct (diamonds) and indirect (circles) bandgaps for $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions according to literature [17,18,173,175,178,182] and Publication II for comparison. Calculated values are given as empty circles with crosses. (b) Zoomed-in image in the compositional range from 89% to 100% of Sb_2S_3 .

These studies show a general increase in bandgap of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems with Sb content, for direct bandgaps – from 1.4–1.6 eV for Bi_2S_3 to 1.5–2.2 eV for Sb_2S_3 . Indirect bandgaps for the same systems were calculated and expected to follow the same trend, but were not assessed experimentally before the studies included in this thesis. The calculated values for indirect bandgaps, given by Mao et al [17], were confirmed in practice in this work (Publication II). Most of the bandgap studies were conducted on the chemically-grown crystals or thin films, with the only exception being a report of thermal evaporation deposition of S-deficient solid solution thin film [18].

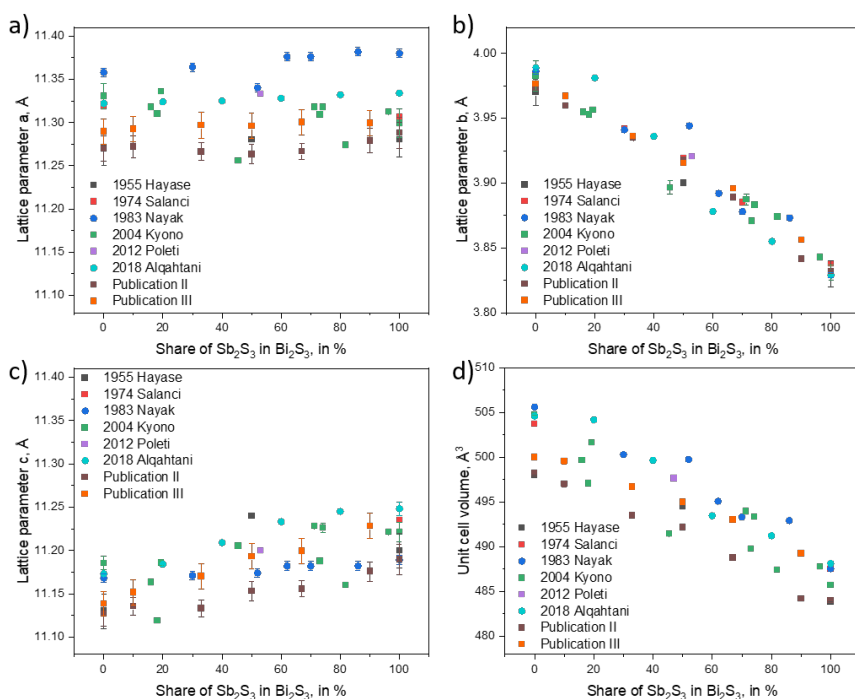


Figure 9. (a-c) Lattice parameters and (d) unit cell volume of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions according to the literature [167,169,172,173,177,184,185], Publication II and Publication III for comparison. Physical synthesis is marked with squares, chemical synthesis with circles.

The six structural studies summarized in Figure 9 show that the lattice parameters of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ change continuously with composition, consistent with Vegard's law. The unit cell volume decreases near-linearly from $\sim 497\text{--}505 \text{ \AA}^3$ for Bi_2S_3 to $\sim 484\text{--}490 \text{ \AA}^3$ for Sb_2S_3 . The largest relative change occurs along the lattice parameter b , which is the main contributor to the change in the unit cell volume. The volume contraction is consistent with the substitution of Bi^{3+} by the smaller Sb^{3+} cation [167]; the increase in c , despite the smaller cation, reflects an anisotropic structural response attributed to the inert-pair effect of the $\text{Sb } 5s^2$ electrons [167]. These trends are established from bulk crystals, powders, and chemically synthesized nanorods, whereas physically deposited thin films have not been previously studied.

From a structural point of view, there are clear complications in characterizing the crystal structure of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions. Both materials are orthorhombic with minor differences in the structural parameters. In terms of crystallographic X-ray diffraction (XRD) data, it results in very similar diffraction patterns for both materials [172,167,185,188] and overlapping of the most prominent reflections. It makes it harder to define the orientation of a polycrystalline film using the texture coefficient (TC) and related approaches, creating a need for more in-depth texture investigation by XRD, specifically pole figure analysis.

There is a limited amount of research on the physical techniques of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution synthesis or deposition of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films [18,165–167,171,184,185]. In the first paper on $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution, Takahashi reported the data on physically-synthesized solid solutions [165], exploring the intersolubility of Sb_2S_3 and Bi_2S_3 , and his findings were proven on physically-grown solid solutions by Springer and LaFlamme [166] in 1972, more than half a century later. First XRD characterization of physically-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions was conducted by Salancı, providing the information about the near-linear changes of lattice parameter b with changes in $[\text{Sb}]:[\text{Bi}]$ ratio [184]. The first in-depth work regarding the structural properties of physically-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution single-crystal grains was published in 2004 by Kyono and Kimata [167]. Crystals were synthesized similarly to [166], except for the temperatures, resulting in a homogeneous elemental distribution throughout the crystal. XRD patterns from the work of Kyono and Kimata were added to the ICSD - Inorganic Crystal Structure Database (cards 01-075-4016 - 01-075-4024), remaining the primary sources of structural information on $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ materials. The only legacy paper on thin films deposited by physical techniques (in this case, vacuum evaporation) describes deposition from the preliminary-alloyed material [18]. However, the synthesized material reported in this paper, according to EDX analysis, had a composition of $\text{Bi}_{0.78}\text{Sb}_{0.95}\text{S}_{4.1}$, indicating issues at the synthesis or measurement stage, rendering the result unreliable.

In terms of applications, $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions have gained attention mostly in energy storage as anode materials [177,183] and in photocatalysis [180] for the improvement of TiO_2 nanotube photoelectrochemical properties. On the PV side, most of the research in this area was conducted in the form of Bi doping of Sb_2S_3 , up to 1.25–2.8% Bi on the Sb sites in Sb_2S_3 lattice [17,178]. The most elaborated paper about both $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films and the corresponding PV devices discusses the Sb_2S_3 with 0.9%, 1.9%, and 2.8% of cations substituted by Bi doping [17], with maximum PCE of 5.2%. However, these films are deposited via the hydrothermal method and cover the very narrow range of $[\text{Sb}]:[\text{Bi}]$ ratios. Phase separation of Sb_2S_3 and Bi_2S_3 at the shares of Bi above 2.8% was reported, which was, however, not discussed in the papers regarding physical synthesis methods.

In summary, the previous $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution studies analyzed structural, optical, and electrical properties of these solid solutions, but the available research remains sparse and unevenly covers different synthesis methods (Figure 7, Table 3). The existing studies – predominantly on chemically-deposited thin films or bulk-synthesized crystalline samples – have established the composition-related trends in lattice parameters and optical bandgap, while the sublimation thermodynamics and properties of physically deposited thin films had not been addressed. PV applications have been limited to Bi-doped Sb_2S_3 within a narrow compositional range [17,178], and no $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films had been deposited by close-spaced sublimation prior to the present work.

1.5. Thin-film deposition techniques for Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$

As reviewed in Sections 1.3 and 1.4, there is a considerable lack of research in both the deposition of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$. For Bi_2S_3 , the researched thin films were grown by both chemical and physical techniques. The main chemical techniques reported are CBD [143,150], CVD [152,153], ALD [120], spray pyrolysis [151], and spin coating [136], while

among the physical deposition techniques the most represented is TE [130,131,15,133,16,148], accompanied by PVD [132], co-evaporation [134] and hotwall method [142]. Only two studies, based on the physical deposition techniques, were focused on the PV applications of Bi_2S_3 thin films [15,16].

For $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, thin films studies relied predominantly on chemical techniques (Table 3) – dip-dry [172,174], CBD [178], arrested precipitation [176], solution pyrolysis [175], cation exchange [182], and hydrothermal method [17]. Only one study employed the physical deposition technique (TE) [18], indicating a far wider gap in this area, compared with Bi_2S_3 .

Since it is difficult to control the nanoribbon orientation of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ while depositing via chemical approaches that dominate the literature, this study is focused on the physical deposition techniques.

It is possible to classify them in two clusters on the basis of the material transport mechanism – sputtering techniques, in which the source material is knocked out from the source tablet by high-energy ions, and vapor transport techniques, where source material is thermally evaporated and transported to the substrate in a vapor phase [189]. Both types of techniques were actively researched as the means of deposition for Q1D materials. Also, both require high-vacuum deposition conditions ($\sim 10^{-1} - 10^{-4}$ Pa), which improves purity, morphology, and texture of the thin films while increasing manufacturing costs compared with chemical techniques [13,190]. In this part, sputtering, thermal evaporation (TE and RTE), vapor transport deposition (VTD), and, with special attention, a close-spaced sublimation (CSS) technique are described.

Sputtering is a widely used family of techniques, which includes magnetron sputtering, radiofrequency (RF) sputtering, ion beam sputtering, etc., with the main difference being the mechanism of the ejection of atoms from the source [191,192]. Both magnetron sputtering [60,193] and RF sputtering [194,195] were actively used for Sb_2Se_3 deposition for PV applications, requiring a post-deposition treatment step. **In thermal evaporation (TE)**, the source material is first heated to its melting point and then evaporated [196]. The further development of TE, **rapid thermal evaporation (RTE)** shares the same principle, but focuses on increasing the deposition rate, which is known to be beneficial for the film's morphology [73]. TE and RTE are widely used for Sb_2Se_3 [59], Sb_2S_3 [197,198], Bi_2S_3 [15,16], and TE is the only physical technique used for $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin-film deposition before this study [18]. **Vapor transport deposition (VTD)**, or horizontal deposition, is a rapid deposition approach previously employed in the CdTe field [199]. In VTD, a quartz tube is used as a deposition volume, where the source material is evaporated from its crucible and transported to the substrate with the carrier gas flow. Source and substrate are located in different, separately controlled temperature zones; the distance between them may be changed, and the carrier gas flow and composition (usually N_2 , Ar, or He) may be specifically selected, which grants a significant degree of flexibility to this technique. It allows the selection of specific deposition conditions, most suitable for the columnar growth in Q1D materials [98,190,200,201]. VTD may be specifically sensitive to substrate morphology [69].

1.5.1. Close-spaced sublimation (CSS)

The concept of CSS is very similar to VTD – the source material, sublimed from the heated source area of the reactor, travels to the colder substrate, with transport controlled by

diffusion and the temperature gradient. Crystallization of the material is predominantly controlled by the substrate temperature. The substrate is usually in close proximity to the source (2-30 mm), which explains the name of the technique. Both source holder and substrate cover serve as susceptors and distributors of the radiative heating, conducting the heat to the source (usually, powder or pellets) and the substrate, respectively [202] (Figure 10). Growth rates in CSS (up to 1-2 $\mu\text{m}/\text{min}$) are usually [164] higher than those of VTD [203]. CSS deposition is generally conducted at constant vacuum [85], whereas in some experiments, inert gases were supplied into the chamber [204]. Among the advantages of the CSS deposition technique is the promotion of columnar grain morphology and the vertical orientation of nanoribbons in Q1D materials (along [010] direction) [30,164,201].

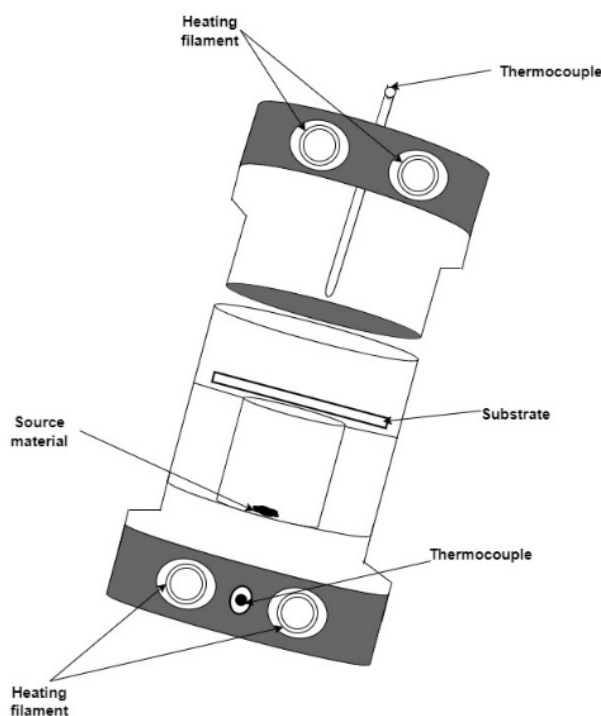


Figure 10. A schematic depiction of the employed CSS reactor [205].

Compared with other physical deposition techniques, CSS is a simpler technique [164] reported [5,154,164,206,207] as able to provide the thin films with more stoichiometric chemical composition [142], lower defect density [207], and more vertical nanoribbons [164,206]. Simplicity of the technique, the near-ampoule conditions within the reactor, and fewer phase transitions than in the TE or RTE, provide more controllable deposition conditions [164]. This makes the technique particularly well-suited as a reference point: observed trends can be, with a higher confidence, attributed to material behavior rather than to deposition artifacts, providing a cleaner basis for establishing the relationship between the deposition conditions (substrate temperature, source temperature, and

their derivatives) and the properties of the resulting thin film. In the prior research, this opportunity was fully missed, being the clear knowledge gap to be filled.

CSS was actively used in CdTe deposition [29,30,163,164] with the following development in Q1D materials – Sb_2S_3 [12,13,208,209] and Sb_2Se_3 [12,204,206,210,211]. One of the early papers about Bi_2S_3 featured the deposition by the hot wall method, which is similar to CSS; however, the amount of data was limited [142].

In the frame of this study, a custom-made hot-wall CSS reactor was employed, with construction identical to that previously used in [12,13,30,164]. The body of the reactor consists of two graphite blocks that enclose the reactor volume and supply heat from the heating elements (tungsten coils) to the source material, the substrate, and the reactor walls. The temperatures of the source and the substrate are separately controlled by thermocouples. The reactor's inner volume is a cylinder with quartz walls, a graphite bottom (which serves as a holder for the source material), and a glass substrate as the top surface. The diameter of the reactor's inner volume is 18 mm, and the distance between the source and substrate is 20 mm.

Summary of the literature review and aims of the thesis

The main points of the literature review with identified knowledge gaps are the following:

1. Quasi-one-dimensional (Q1D) emerging PV materials, such as $(\text{Sb}_x\text{Bi}_{1-x})_2(\text{S}_y\text{Se}_{1-y})_3$, are promising absorber materials due to benign grain boundaries. Unlike Sb_2S_3 , Sb_2Se_3 , and $\text{Sb}_2(\text{S}_y\text{Se}_{1-y})_3$, which were actively researched for PV applications, achieving the PCEs of 8.36%, 10.58%, and 11.02%, respectively, the Bi-based materials (in particular, Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$) are deeply understudied despite the similarities with the Sb-based ones and the benefits, such as the lower toxicity of bismuth compared with antimony.
2. Bi_2S_3 is an orthorhombic material, sharing similarities with Sb-based chalcogenides, but being mostly n-type material with low resistivity ($\sim 10 \text{ Ohm}\cdot\text{cm}$). Structurally, Bi_2S_3 is similar to Sb_2S_3 and Sb_2Se_3 , with the same orthorhombic structure and similar lattice parameters. Unlike them, Bi_2S_3 exhibits predominantly n-type conductivity and a mostly indirect bandgap. The majority of research on Bi_2S_3 for PV or photocatalysis is conducted on chemically deposited coatings, nanorods, and nanocrystals, with very few studies on physical deposition. In almost all studies, TE and RTE deposition techniques are applied. The CSS deposition of Bi_2S_3 , including suitable deposition conditions and the properties of the deposited thin films, has not yet been investigated. Additionally, there are only two works on Bi_2S_3 -based solar cells with a Bi_2S_3 layer deposited by physical deposition techniques, both using TE-related techniques.
3. Bi_2S_3 -based solar cell studies are scarce compared with the studies of Sb-based chalcogenides, with approximately 10 papers on Bi_2S_3 solar cells. Only in two of them was the physical deposition of Bi_2S_3 reported, by TE and RTE deposition techniques, respectively. CSS is recognized as a promising technique for Q1D material deposition, but the use of a CSS-deposited Bi_2S_3 thin film as a solar cell absorber has not yet been reported.

4. PCEs of Bi_2S_3 devices have not exceeded 4.87%, with the absorbers mainly deposited by chemical techniques as nanocrystals and nanorods. Other Q1D chalcogenide materials, when deposited via physical techniques, tend to exhibit improved morphology and texture compared with chemically deposited ones.
5. The number of reports in the literature on PL studies of Bi_2S_3 physically deposited thin films is limited – just two studies have reported room-temperature PL, while the temperature-dependent PL studies have not been reported. This leaves the defect structure of Bi_2S_3 in physically deposited thin films understudied. Six defect states in Bi_2S_3 were theoretically calculated, and two of them (of V_{Bi} and S_i) were revealed by room temperature PL.
6. Solid solutions of Bi_2S_3 with Sb_2S_3 , $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, are a highly interesting group of materials, which provides a wide selection of optoelectronic properties (conductivity type, resistivity, and bandgap). However, the entire body of knowledge on $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ materials was limited to 20-25 papers by 2022. Only one study reported physical thin-film deposition by RTE; in all other cases, chemical thin-film deposition techniques were employed. Melting temperatures, lattice parameters, and bandgaps for $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions near-linearly change from Bi_2S_3 to Sb_2S_3 , with no rapid changes or extremum points yet reported.
7. There is only one paper on $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solar cells, with the highest Bi_2S_3 content in the absorber material at 2.8 at%. No studies involving more bulk $[\text{Sb}]:[\text{Bi}]$ ratios have yet been published.
8. Texture (nanoribbon orientation) is critical for the functioning of Q1D thin-film PV material. Studies with in-depth characterization of texture aimed at finding optimal deposition conditions have been published for Sb_2Se_3 and Sb_2S_3 , but not for Bi_2S_3 and, especially, $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$. Physical deposition techniques provide a higher degree of control over the nanoribbon orientation in the deposited Q1D materials; however, there were no attempts in the literature to try this way of exploring the material properties of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$.

Based on these findings, **the aim of this thesis is** to develop the CSS deposition protocols for Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ (with different $[\text{Sb}]:[\text{Bi}]$ ratios) and provide an understanding of the impact of CSS deposition conditions on thin-film properties, including the morphological, structural, and optoelectronic parameters of the films, and demonstrate their applicability in solar cells.

To achieve this aim, the following **objectives** were set:

1. Systematically investigate and identify the optimal CSS deposition parameters for Bi_2S_3 thin films on glass substrate.
2. Explore the existence of defect states in Bi_2S_3 by means of low-temperature photoluminescence measurements to provide the first in-depth defect study for physically deposited Bi_2S_3 thin films.
3. Synthesize a series of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions with 5 different $[\text{Sb}]:[\text{Bi}]$ ratios and use the resulting solid solutions as source materials for thin films, characterizing both source materials (powders) and thin films.
4. Optimize the CSS deposition conditions for all studied $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions, exploring the dependence of their morphology, structure, texture, and optoelectronic properties on $[\text{Sb}]:[\text{Bi}]$ ratio and deposition conditions.

5. Produce the proof-of-concept thin-film solar cells with Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ absorbers to show the current stage of the applicability of these materials in PV.
6. Conduct an in-depth characterization of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin film texture by means of Bragg-Brentano XRD (BBXRD) (applying TC and RCT analytical approaches), texture XRD, and Grazing-incidence XRD (GIXRD), and systematically investigate the trends in nanoribbon orientation with regard to the CSS deposition conditions.

2 Experimental

This chapter describes the synthesis of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions, the CSS deposition of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, the fabrication of proof-of-concept solar cells, and the analytical techniques employed for their characterization.

2.1. $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution synthesis

$(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions with $x = 0.1, 0.33, 0.5, 0.67, 0.9$ were synthesized from 5N (99.999%) purity Sb_2S_3 and Bi_2S_3 binary precursors under the same synthesis conditions (Publication II). Precursors were weighed in the desired amounts and ratios, ground in the agate mortar, and homogeneously mixed. Then, the powder mixtures were loaded into the quartz ampoules, which were vacuumized to $\sim 1\text{Pa}$ and sealed using an acetylene torch. All five mixtures were heated from RT to 800°C (above the melting points of both Sb_2S_3 and Bi_2S_3) at a heating rate of $10^\circ\text{C}/\text{min}$. After maintaining this temperature for 24 hours, the temperature was decreased with the initial ramp of $8-9^\circ\text{C}/\text{min}$ and the main ramp of $2-3^\circ\text{C}/\text{min}$ down to room temperature.

2.2. Thin film fabrication

2.2.1. Substrate preparation

The same substrate preparation protocol was employed in Publications I-III. For both thin films on glass and solar cells (Section 2.3), fluorine-doped tin oxide (FTO) coated glass substrates from Sigma Aldrich were used (soda-lime glass thickness $\sim 2.3\text{mm}$, FTO thickness 200 nm, sheet resistance $\sim 7\ \Omega/\text{Sq}$), with the glass side used for most of the samples, while the FTO side was used only for solar cells. Glass/FTO plates were cut into $20\times 20\text{ mm}$ squares. Cut substrates were placed into a degreasing solution (10 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), 10 ml of deionized water, and 100 ml of concentrated sulfuric acid (H_2SO_4)) for 3 hours [160]. At the next step, the glass/FTO substrates were rinsed and boiled in distilled water, then dried with a hot gun and kept in a desiccator until usage.

2.2.2. CSS deposition of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ absorber thin films

In Publications I-III, Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films were deposited using a custom-made CSS system (Figure 10), using as source materials the ground lump of Bi_2S_3 , Sb_2S_3 (purchased from Sigma-Aldrich and ThermoScientific), and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions (synthesized according to 2.2). The experimental details of CSS deposition conditions are summarized in Table 4. Deposition was conducted at a pressure of 10^{-4} Pa .

Table 4. Experimental details on Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films by CSS. The table outlines the substrate, source material, seed layer inclusion, CSS deposition conditions (T_{so} , T_{sub} , deposition time), and the final sample stack (for both material and device characterization).

Publication	Substrate	Source material	Seed layer	Absorber deposition parameters			Sample stack
				T_{so} , °C	T_{sub} , °C	Dep. time, min	
I	Roughened glass	Bi_2S_3 5N purity, Sigma-Aldrich	No seed layer	450	100	1 - 5	Rough glass/ Bi_2S_3
	Flat glass Glass/FTO/CBD-CdS Glass/FTO/USP-TiO ₂			- 600	- 550		Glass/ Bi_2S_3 Glass/FTO/CBD-CdS/ Bi_2S_3 Glass/FTO/USP-TiO ₂ / Bi_2S_3
II and III	Flat glass Glass/FTO/CSS-CdS	Bi_2S_3 and Sb_2S_3 5N purity (Sigma-Aldrich and ThermoScientific), $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions with $x = 0.1, 0.33, 0.5, 0.67$, and 0.9 from the same binary materials	No seed for Bi_2S_3 and Bi-rich; With a seed layer for Sb_2S_3 and Sb-rich	460 - 510	280 - 430	1 - 60	Glass/ $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ Glass/FTO/CBD-CdS/ $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ Glass/FTO/USP-TiO ₂ / $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$

2.3. Solar cell fabrication

For solar cell devices, the fabrication procedure included substrate (glass/FTO) preparation (Section 2.2), ETL (CdS or TiO₂) deposition, Bi-based absorber material deposition by CSS, and Au back contact deposition by thermal evaporation. The schematic depictions of the PV devices obtained in this work are given in Figure 11.

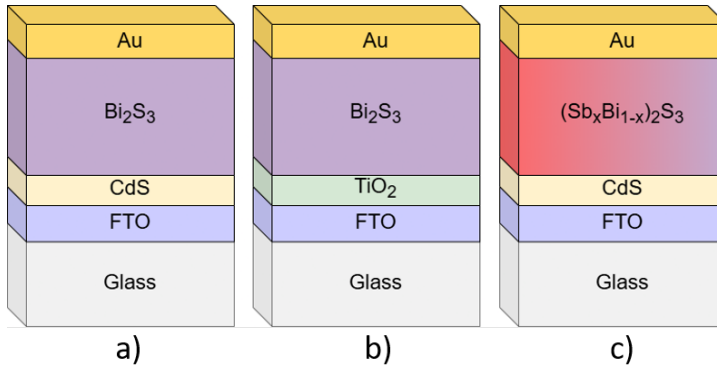


Figure 11. Sample stacks used in the studies: (a) glass/FTO/CBD-CdS/ Bi_2S_3 /Au and (b) glass/FTO/USP-TiO₂/ Bi_2S_3 /Au (in Publication I), (c) glass/FTO/CSS-CdS/ $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ /Au (in Publications II and III).

In Publication I, two ETL configurations were investigated for Bi_2S_3 solar cells: TiO_2 thin films (100–200 nm) deposited onto FTO by ultrasonic spray pyrolysis (USP) at 350 °C, following the protocols established in [212], [213], and CdS thin films (80–100 nm) deposited onto FTO by chemical bath deposition (CBD), following [214,215]. Post-deposition treatment of TiO_2 involved two 30-minute annealing steps (120 °C under vacuum, then 450 °C in air); CdS was annealed at 120 °C under vacuum for 1 h. In Publication II, CdS ETL films (80–120 nm) were deposited onto FTO by CSS at $T_{\text{so}} = 600$ °C and $T_{\text{sub}} = 320$ °C for 5 minutes using CdS powder (Sigma-Aldrich, 5N purity) at a pressure of 10^{-4} Pa. Detailed ETL preparation protocols for each configuration are described in the respective publications.

Au back contacts were deposited by TE from gold wire (Alfa Aesar) through a mica mask at a pressure of 10^{-4} Pa, completing the glass/FTO/ETL/absorber/Au device stacks (Figure 11).

2.4. Characterization

Characterization techniques for solid solutions, thin films, and solar cell devices are briefly summarized in this section. Unless stated otherwise, the measurements were conducted at the Department of Materials and Environmental Technology, Tallinn University of Technology.

Scanning electron microscopy (SEM) and adjunct techniques (EDX, EBSD)

The morphology of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films was assessed using SEM analysis. For Publications I and II, the images were made at Tallinn University of Technology by Zeiss HR-SEM MERLIN equipped with a GEMINI II column by Dr. Olga Volobujeva and Dr. Valdek Mikli (Tallinn University of Technology). For Publication III, the Zeiss UltraPlus system SEM setup was used, equipped with an Oxford Instruments Symmetry EBSD detector and operated by Dr. Daniel Abou-Ras from Helmholtz-Zentrum Berlin for Materials and Energy. Both systems were coupled with Energy-Dispersive X-ray Spectroscopy (EDX), used for compositional analysis of the thin films at both cross-section and top-surface projections.

For Publication III, the local texture was characterized using Electron Backscatter Diffraction (EBSD). The orientation mapping was done using a Zeiss UltraPlus scanning electron microscope equipped with an Oxford Instruments Symmetry EBSD detector. The measurements were conducted at a beam energy of 20 keV and a beam current of about 6 nA, using the acquisition and evaluation software AZtec. The EBSD and EDX mappings for Publication III were conducted by Dr. Daniel Abou-Ras from Helmholtz-Zentrum Berlin for Materials and Energy.

X-ray fluorescence (XRF) chemical analysis

XRF characterization, which provided the chemical data to complement the EDX findings, was conducted on a Bruker M4 Tornado spectrometer at Helmholtz-Zentrum Berlin for Materials and Energy.

Hall measurement

Electrical properties of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, such as resistivity, mobility, and charge concentration, given in Publications I and II, were measured at room temperature using MMR's Hall system and a Hall and van der Pauw controller H-50. The thickness of the films was estimated from cross-section SEM images and entered into the software.

As contacts, Indium pads were used. Each film was measured at least five times to reduce the error.

Ultraviolet-visible spectroscopy (UV-Vis)

In Publications I and II, the optical bandgaps (E_g) of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films were extracted (using Tauc plots) from the total transmittance and reflectance spectra using an ultraviolet-visible-near infrared spectrophotometer Jasco V-670 over the 300-1500 nm range.

Photoluminescence (PL)

Low-temperature photoluminescence (PL) measurements were used to reveal the defect structure of the Bi_2S_3 (Publication I) and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ (Publication II) thin films.

In Publication I, the ionization potential and electron affinities of the thin films in the device stack were determined by the photoelectron emission spectroscopy technique to ascertain the band alignment. A 0.64 m focal length single grating (600 mm^{-1}) monochromator and the 442 nm line of a He–Cd laser with different powers were used for PL measurements. A Hamamatsu InGaAs photomultiplier tube was used to detect the PL signal from the Bi_2S_3 thin films. A closed-cycle helium cryostat was employed to measure the temperature dependencies of the PL spectra at temperatures from 20 to 300 K. The laser spot size for these measurements was 0.2 mm in diameter. Dr. Taavi Raadik (Tallinn University of Technology) carried out the PL measurements on Bi_2S_3 .

In Publication II, the PL characterization was conducted using two lasers - DPSS 266 nm pulsed laser (SNU-20F-100, *Teem Photonics*TM) with repetition rate 19 kHz, constant pulse width range (FWHM) 0.6 ns, laser spot diameter = 0.32 mm; and DPSS 532 nm CW laser (MGL-III-532, *CNI*) with laser spot diameter = 0.21 mm. In both cases, the intensity was varied using a neutral density gradient filter. PL detection was done with a conventional lock-in system - thermoelectrically cooled InGaAs (IGA-030_TE2-H, *EOS*) photodetector (set on glass - 266 nm measurements) and liquid nitrogen cooled InGaAs (IGA2.2-010-LN, *EOS*) photodetector (set on glass - 532 nm measurements, set on CdS – 266nm and 532 nm measurements). For temperature control, samples were mounted on the cold finger of a closed-cycle He cryostat (*JANIS*) coupled with a temperature controller (*Lakeshore*). PL measurements on $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films were performed by Dr. Evelina Dudutienė from the State Research Institute Center for Physical Sciences and Technology of Lithuania.

Raman spectroscopy

In Publication I, the phase composition of Bi_2S_3 was studied with a Horiba Jobin Yvon Labram HR 800 spectrometer ($\lambda = 532\text{ nm}$) in Tallinn University of Technology, with the help of Dr. Reelika Kaupmees.

In Publication II, the phase composition of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films was studied using an FHR 640 monochromator from Horiba, coupled with a CCD detector. A solid-state laser with a 532 nm emission line was used as an excitation source, setting the power at $\sim 1\text{ mW}$ over a $\sim 70\text{ }\mu\text{m}$ diameter spot. The measurements were performed in a backscattering configuration through a special probe designed in IREC. Up to 16 points were assessed in each sample, revealing information about lateral homogeneity in the thin films. All spectra were normalized to the position of the main peak of monocrystalline Si by imposing its peak to 520 cm^{-1} . The measurements were performed by Dr. Maxim Guc and Victoria Rotaru at the Catalonia Institute for Energy Research (IREC).

X-ray diffraction (XRD) techniques – BBXRD, GIXRD, texture XRD

The crystal structure and texture of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films were analyzed by a comprehensive set of XRD-based techniques. The XRD measurements for Publication III were conducted in close collaboration with Dr. René Schwiddessen from Helmholtz-Zentrum Berlin for Materials and Energy.

Bragg-Brentano XRD

Bragg-Brentano XRD (BBXRD) measurements for Publications I-III were conducted using the Rigaku Ultima IV diffractometer, complemented for Publication III with the measurements on the Bruker D8 diffractometer, both with $\text{Cu } K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA). For Publications I and II, PDXL2 software was used for BBXRD data analysis. For Publication III, Le Bail analysis [216] was conducted for both BBXRD and GIXRD data to obtain the lattice parameters using FullProf software [217].

Grazing-incidence XRD (GIXRD)

Grazing-incidence XRD (GIXRD) measurements for Publication III were performed using a PANalytical X'pert Pro MPD diffractometer with $\text{Cu-}K_{\alpha 1}$ -radiation ($\lambda = 1.54 \text{ \AA}$). To obtain depth profile information, the grazing angle was set at 0.5° , 2.5° , and 5° for Bi_2S_3 and solid solutions up to $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ and at 0.5° , 1.5° , and 3° for the $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ solid solutions, to get the structure information about the regions at the approximate depth of 65-85 nm, 240-370 nm, and 475-750 nm, respectively, similarly to the procedure in [53]. Le Bail analysis was used to obtain lattice parameters and microstrain values, using FullProf software [217].

Texture XRD

Texture XRD analysis for Publication III was conducted using a PANalytical X'Pert Pro MRD X-ray diffractometer equipped with an Eulerian cradle employing two-axis scans along ϕ and χ in increments of 5° each. The intensity distribution was recorded along full circles (from 0° to 360°) and at different sample tilts (from 0° to 85°).

Solar cell characterization

The current density – voltage (J-V) characteristics of solar cell devices were measured at room temperature in ambient air under standard AM1.5G illumination (100 mW/cm^2). J-V curves were recorded using an AUTOLAB PGSTAT 30 potentiostat. In Publication I, a Wavelabs LS-2 LED solar simulator was used; in Publication II, an Oriel class A solar simulator 91159 A was used. External quantum efficiency (EQE) spectra were measured in the 300–1100 nm wavelength range using a monochromatized light source (Newport 300 W Xenon lamp, Newport Cornerstone 260 monochromator), a Merlin digital lock-in detector, and a factory-calibrated Si reference detector.

3 Results and discussion

In this chapter, the main results obtained in Publications I-III are presented. The first section (3.1) focuses on the fabrication and characterization of Bi_2S_3 thin films on various substrates and Bi_2S_3 -based thin-film solar cell devices. Section 3.2 is dedicated to the synthesis, thin-film deposition, and characterization of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions, as well as the properties of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ -based proof-of-concept thin-film solar cell device. Section 3.3 examines the structural properties of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films, characterized using an ensemble of X-ray-based characterization techniques.

3.1. Bi_2S_3 by close-spaced sublimation

In this section, the first study on CSS deposition of Bi_2S_3 , the performance of Glass/FTO/CBD-CdS/ Bi_2S_3 and Glass/FTO/USP-TiO₂/ Bi_2S_3 , and the first temperature-dependence PL study of Bi_2S_3 thin films are discussed. The results presented here have been published in Publication I.

3.1.1. Structural properties of Bi_2S_3 thin films

Bi_2S_3 films were deposited by CSS onto four different substrates – roughened microscopic glass, plain glass on the backside of FTO substrate, glass/FTO/TiO₂ (further just TiO₂), and glass/FTO/CdS (further just CdS) stacks. A large set of Bi_2S_3 absorber layers was initially deposited on roughened glass substrate with the aim of identifying the optimal CSS source (T_{so}) and substrate temperatures (T_{sub}) which would allow a reasonable deposition rate and lead to the formation of compact and dense films. The roughened glass plates with a root-mean-square roughness, R_q , of 2.66 nm (Sigma-Aldrich) were used to ensure better adhesion of the Bi_2S_3 absorber films and also to perform electrical measurements. After identifying the optimal source temperature, the absorber was deposited onto different substrates (including plain glass, TiO₂/FTO/glass, and CdS/FTO/glass) at substrate temperatures ranging from 200 to 450 °C in steps of $\Delta T = 50$ °C. Information about deposition conditions for different substrates is summarized in Table 5. All Bi_2S_3 films deposited on various substrates were first characterized by XRD and Raman spectroscopy. Figure 12.a,c,e shows XRD patterns of Bi_2S_3 films deposited onto roughened glass, which were indexed and assigned to orthorhombic Bi_2S_3 crystal structure with $Pbnm$ space group symmetry (JCPDS 00-017-0320) [218]. Through this section, Miller indices are given in the $Pnma$ notation adopted as standard in this work (Section 1.2).

Table 5. Deposition conditions for various substrates.

Substrate	Roughened glass	Plain glass	TiO ₂	CdS
T_{so} , °C	450, 500, 550, 600	550	550	550
T_{sub} , °C	100-550	200-450	200-450	200-450
Deposition time, min	1	1, 2, 3, 5	1	1

For a better qualitative analysis of the preferential orientation of the crystallite along specific crystalline planes, the texture coefficient (TC) was calculated (Figure 12.b,d,f) according to Eq. (1):

$$TC(hkl) = \frac{I(hkl)}{I_0(hkl)} \times \left[\frac{1}{N} \sum_{i=0}^N \frac{I(hkl)}{I_0(hkl)} \right]^{-1} \quad (1)$$

where $I(hkl)$ is the measured intensity for a given reflection with hkl indices, $I_0(hkl)$ is a reference intensity for a given reflection acquired from the JCPDS Card No. 00-017-0320, and N is the number of reflections considered in the analysis [219].

It can be seen that, for a given T_{so} , the TC values change differently depending on T_{sub} . At T_{so} 500 °C, 200 and 301 crystalline planes were dominant. As the T_{sub} increased, TC values increased for the 200 and 301 planes, while TC values along other major planes, such as 202 and 112, decreased. At T_{so} 550 °C, the most prominent planes were 301, 103, and 112. Generally, it was difficult to discern a clear trend in the TC of 200, 202, and 301 planes, whereas the TC of 103, 112, and 212 planes increased slightly with increasing T_{sub} . At T_{so} 600 °C, the most prominent planes were 103, 112, and 212, for which the TC values increased systematically when the T_{sub} increased from 200 to 350 °C. For the same T_{so} , at substrate temperatures higher than 350 °C, the TC values of the same planes decreased.

For the next set of samples in which the Bi_2S_3 films were deposited on glass, CdS, and TiO_2 , the T_{so} 550 °C was chosen as the optimal source temperature, allowing an optimal deposition rate of $\sim 0.8\text{-}1\mu\text{m/min}$. The choice of this temperature was also based on systematic source temperature screening across different substrates, and, according to XRD data, the 550 °C source temperature yielded the most pronounced orientation of the crystallite along (hkl , $k=1$). In addition, compared to T_{so} 600 °C, T_{so} 550 °C provided better controllability of the CSS deposition process and absorber layer thickness.

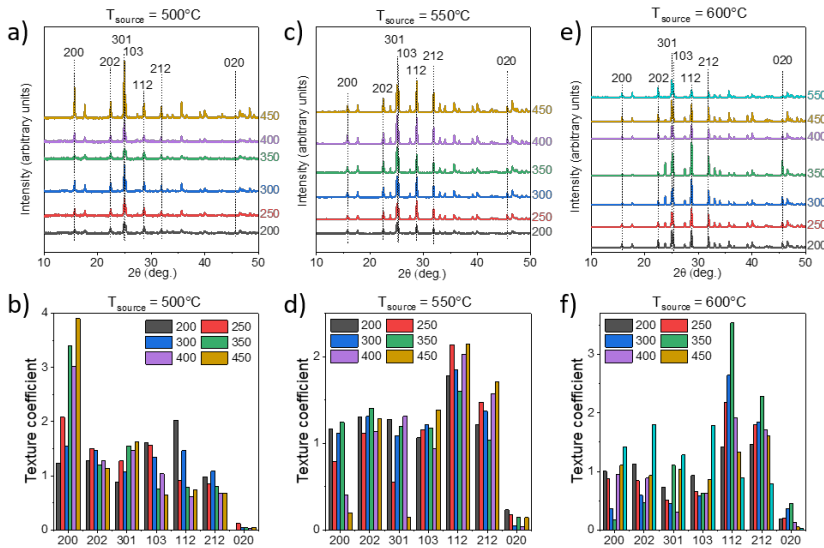


Figure 12. XRD patterns of Bi_2S_3 absorber films deposited by CSS onto roughened glass substrates, at three source temperatures (T_{so}) – (a) 500 °C, (c) 550 °C, (e) 600 °C, and for each T_{so} , the substrate temperature varied between 200 °C and 550 °C in steps of $\Delta T = 50$ °C; (b, d, f) The corresponding TC values calculated from integrated intensity ratios for main crystal planes in Bi_2S_3 films.

When performing the TC analysis of Bi_2S_3 deposited onto plain glass (Figure 13.a,b) substrates at T_{so} 550 °C, no clear trend was found, except for the decrease in TC for the 212 plane with the increase in substrate temperature from 250 to 450 °C. At the same time, in comparison with the films deposited onto rough glass there is a difference in the TCs of the films grown onto plain glass. This effect can be explained by different surface energy of these two substrates. In the case of rough glass, the higher surface energy can provide different conditions for the nucleation sites and adatom diffusion on the surface. This will affect the formation of islands, their coalescence, and grain coarsening during the film growth and thus the orientation of the final grains in the layers. For the absorber deposited on TiO_2 substrates (Figure 13.c,d), as the substrate temperature increased, the TCs decreased for the 200, 202, 301, and 103 planes while increasing for the 212 plane. In the case of Bi_2S_3 films deposited on CdS substrate (Figure 13.e,f), the TC was slowly decreasing for 301 and 112 planes and increasing for 103 and 212 planes, as the substrate temperature increased from 250 to 450 °C.

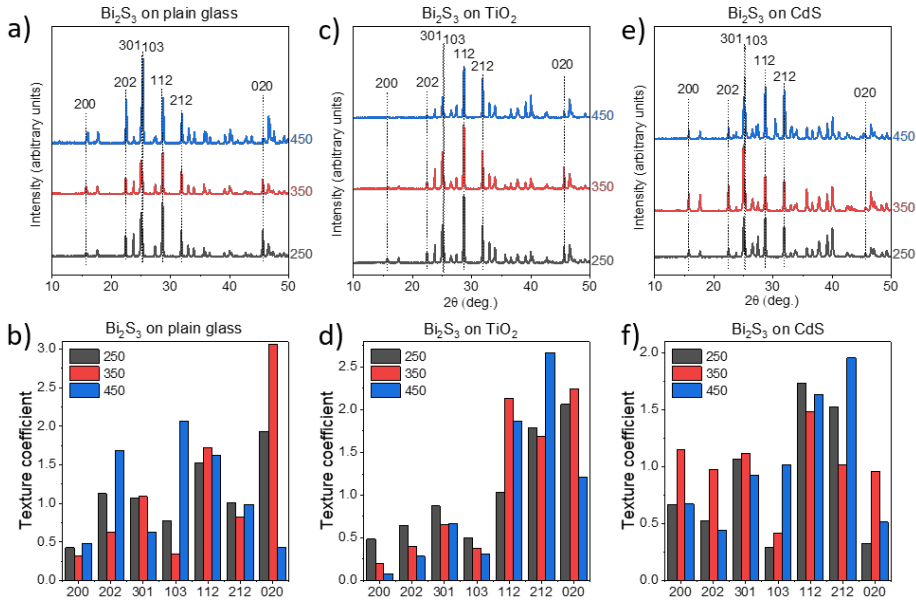


Figure 13. XRD patterns of Bi_2S_3 absorber films deposited by CSS at T_{so} 550 °C and T_{sub} 250 °C, 350 °C, and 450 °C onto various substrates – (a) plain glass, (c) TiO_2 , and (e) CdS; (b, d, f) TC values calculated from integrated intensity ratios for main crystal planes in Bi_2S_3 films on respective substrates.

According to XRD results, at T_{so} below 500 °C, the film appeared mostly amorphous, with only a few distinguishable reflections (Publication I). On the other hand, it was observed that in the XRD pattern of Bi_2S_3 deposited with $T_{\text{so}} \sim 600$ °C and $T_{\text{sub}} \sim 450 - 500$ °C, separated phases of Bi and Bi_2S_3 were detected (Publication I), suggesting that at higher deposition temperature, there was an excessive loss of sulfur from the system. Such a phenomenon can be explained by the higher partial pressure of sulfur at $T \geq 600$ °C, which readily generates sulfur-poor conditions in the Bi_2S_3 system [161].

It should be noted that the phase composition of Bi_2S_3 was further analyzed by Raman measurements, as seen in Figure 14. For the T_{so} 550 °C source temperature, independent of the substrate temperature and the used substrate for the deposition of Bi_2S_3 films, Raman spectra showed similar vibrational modes, which correspond to the pure Bi_2S_3 phase [220].

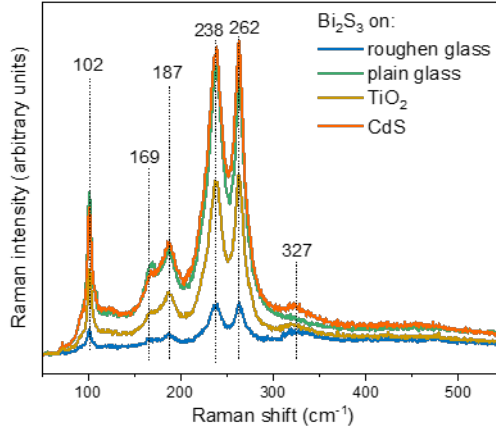


Figure 14. Raman spectra of Bi_2S_3 films on roughened glass, plain glass, $\text{CdS}/\text{FTO}/\text{glass}$, and $\text{TiO}_2/\text{FTO}/\text{glass}$ substrates. Raman spectra of the structures revealed Raman shifts at 101 cm^{-1} , 169 cm^{-1} , 187 cm^{-1} , 238 cm^{-1} , 262 cm^{-1} and 327 cm^{-1} , which correspond to the Bi_2S_3 crystal phase.

Bi_2S_3 absorber films, deposited on all substrates, at low (250 °C) and high (450 °C) temperatures, were analyzed by scanning electron microscopy (SEM). Images of Bi_2S_3 films, deposited onto roughened glass, are given in Figure 15. It can be seen that absorber layers deposited at higher temperatures have larger grains than those deposited at lower temperatures.

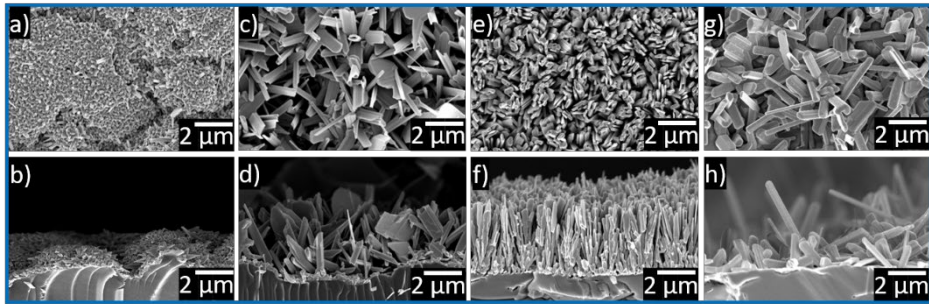


Figure 15. (a, c, e, g) Top-view and (b, d, f, h) cross-sectional SEM images of Bi_2S_3 films deposited onto a roughened glass substrate at substrate temperature (T_{sub}) of (a, b) 200 °C, (c, d) 250 °C at 1 min deposition time, (e, f) T_{sub} of 250 °C at 3 min deposition time, and (g, h) T_{sub} of 450 °C at 1 min deposition time.

At 200 °C, the surface of the substrate was covered with a ~200 nm thick “seed” layer of small randomly-oriented grains (Figure 15.a,b). At higher temperatures (200-350 °C), needles and prism-like grains with no dominating orientation of growth were

observed out of a minor portion of the seed layer (Figure 15.c,d). If the deposition time in this temperature region was prolonged, more and more grains from the seed layer grew into needles (Figure 15.e,f). These needles grew taller and more aligned as the film thickness increased from 3-4 μm to 4-5 μm , resulting from a change in deposition time from 1 min (Figure 15.d) to 3 min (Figure 15.f). At high temperatures (400-450 $^{\circ}\text{C}$), grains tend to coalesce, forming big randomly-oriented "rods", while the previously-existing seed layer is not visible anymore (Figure 15.g,h).

In the case of Bi_2S_3 deposited on plain glass, fewer nucleation centers were available on the substrate surface. This implies that a higher minimum T_{so} was required for the formation of the first Bi_2S_3 thin film on roughened glass, approximately 420 $^{\circ}\text{C}$, compared with plain glass, approximately 470 $^{\circ}\text{C}$. At T_{so} 250 $^{\circ}\text{C}$, the Bi_2S_3 films grow similarly to those on roughened glass (Figure 16.a,b). At T_{so} 450 $^{\circ}\text{C}$, a densely-packed morphology was observed in which grains grow in both lateral and longitudinal directions (Figure 16.c,d). In the case of prolonged deposition time, ~ 200 nm and ~ 600 nm thick films were obtained for 3 min (Figure 16.e,f) and 5 min (Figure 16.g,h), respectively.

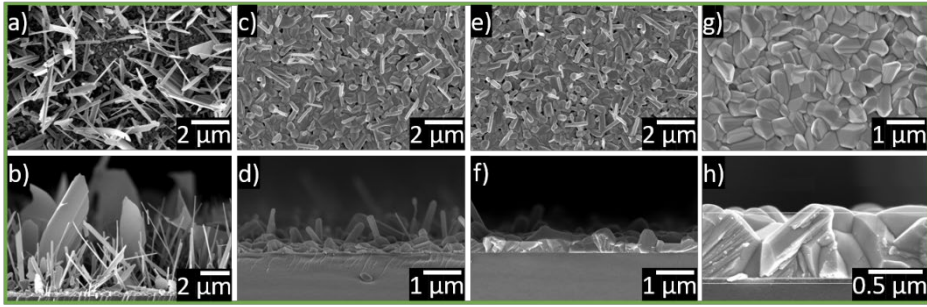


Figure 16. (a, c, e, g) Top view and (b, d, f, h) cross-sectional SEM images of Bi_2S_3 films deposited onto a plain glass substrate at: (a,b) substrate temperature (T_{sub}) of 250 $^{\circ}\text{C}$ at 1 min deposition time; T_{sub} 450 $^{\circ}\text{C}$ at (c,d) 1 min, (e,f) 3 min, and (g,h) 5 min deposition time.

For Bi_2S_3 films, deposited on plain glass, TiO_2 , and CdS at T_{sub} 250 $^{\circ}\text{C}$, a similar morphology in which the films consisted of randomly-oriented needles and a wide distribution by size (0.5-6 μm) was observed (Figure 17). At T_{sub} 450 $^{\circ}\text{C}$, thick films of large, rather columnar grains were observed (Figure 17.d,h), with a similar formation mechanism seen in Figure 17.h. As a result of 1 min deposition, ~ 1 μm thick Bi_2S_3 films were observed onto TiO_2 and CdS substrates, while a five times thinner (200 nm) film was observed on plain glass after 3 times longer deposition. The thicker film on TiO_2 and CdS can be explained by a higher density of nucleation sites on the surface of both TiO_2 and CdS . It should be mentioned that EDX analysis was conducted, focusing on the compositional maps of the cross-section to check the homogeneity of the elemental distribution. No metallic elements or micro-inclusions of secondary phases were detected in the Bi_2S_3 films deposited at T_{so} 550 $^{\circ}\text{C}$ (Publication I).

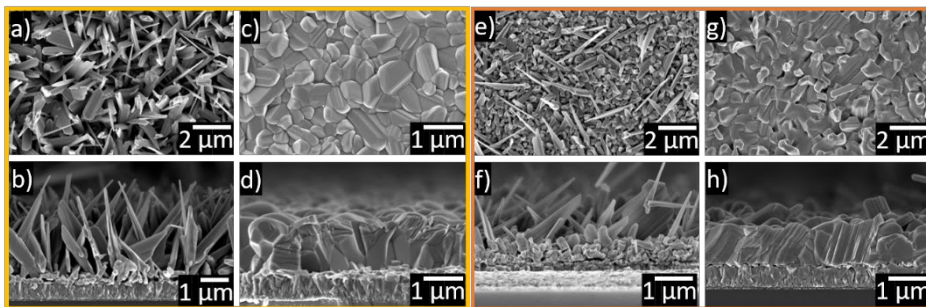


Figure 17. (a, c, e, g) Top view and (b, d, f, h) cross-sectional SEM images of Bi_2S_3 films deposited onto (a-d) TiO_2 and (e-h) CdS substrates, at substrate temperature (T_{sub}) of (a-b, e-f) 250 °C and (c-d, g-h) 450 °C, deposition time is 1 min.

Based on the results of structural and morphological changes of Bi_2S_3 absorber layers depending on the CSS deposition conditions and use of various substrates, the following main conclusions can be drawn:

- i. Within the given set of source and substrate temperature regimes (T_{so} : 450 °C, 500 °C, 550 °C, and 600 °C; T_{sub} : 250 °C, 450 °C), the source temperature of 550 °C and substrate temperature 400-450 °C were identified as optimal temperatures which allowed reasonable deposition rate ($\sim 0.5\text{-}0.8 \mu\text{m}/\text{min}$) and fabrication of uniform Bi_2S_3 films with a suitable (hkl , $k=1$) orientation independent of whether the deposition was performed on either plain glass, TiO_2 or CdS as substrate;
- ii. At T_{so} below the optimal one, independent of the applied substrate temperatures, the absorber grains were predominantly oriented along (hkl , $k=0$), while a high amount of amorphous phase was observed in Bi_2S_3 film grown at T_{so} 450 °C;
- iii. 600 °C source temperature was identified as the critical temperature, generating conditions for sulfur loss in the Bi_2S_3 system with the formation of separated metallic bismuth and Bi_2S_3 phases.

It is widely established for similar emerging inorganic chalcogenides such as Sb_2S_3 and Sb_2Se_3 absorbers that such a preferential (hkl , $k=1$) orientation, obtained at T_{so} 550 °C and T_{sub} 450 °C for Bi_2S_3 film, would be optimal for efficient charge transport and collection in the solar cell [221–224]. Several attempts have investigated the properties of Bi_2S_3 deposited via physical deposition techniques. Employing a thermal evaporation technique at T_{sub} between 25 °C and 285 °C, Haaf et al. [132] found that Bi_2S_3 films grown at temperatures right above the crystallization temperature exhibit a significant overrepresentation of reflections with indices (hkl $k=0$), with a preferred growth along the c -axis parallel to the surface of the substrate. Therein, only structural and optical properties were analyzed without the application of the absorber layer in a solar cell device. Following the same technological approach, Rincón et al. [130] obtained crystalline Bi_2S_3 film at T_{sub} 250-300 °C; however, with substantial contribution in XRD patterns from 104, 012, and 003 planes of metallic bismuth. Therein, the appearance of the separated phase was explained due to the nonstoichiometric dissociation of the S/Bi precipitate. Using a

rapid thermal evaporation technique with a fast deposition rate (0.5 $\mu\text{m}/\text{min}$) at T_{sub} 100-300 $^{\circ}\text{C}$, Song et al. [16] obtained crystalline, 230-, 111-, 221- oriented, compact Bi_2S_3 films. So far, this is the only study in which the Bi_2S_3 film deposited by the physical deposition technique was incorporated in solar cells with a demonstration of proof-of-concept device efficiency of 0.75%.

In terms of CSS processing temperature, our results seem to correlate with the findings by Song et al. [16], with the difference that in our case, the optimal growth condition was identified at a slightly higher substrate temperature and a general trend for the TC favorable towards grain orientation along $(hkl, k=1)$ planes. Having noticed these findings, the next challenge in this study was to apply the absorber, processed with the identified optimal T_{so} and T_{sub} , in a superstrate configuration solar cell with TiO_2 or CdS as the junction partner layer.

3.1.2. Bi_2S_3 device efficiency: analysis of the performance limitations

Based on the above analysis of the systematic structural changes in the Bi_2S_3 film growth depending on the CSS source and substrate deposition temperatures, we further analyzed how these structural changes correlate with the efficiencies of superstrate configuration glass/FTO/ $\text{CdS}/\text{Bi}_2\text{S}_3/\text{Au}$ and glass/FTO/ $\text{TiO}_2/\text{Bi}_2\text{S}_3/\text{Au}$ thin-film solar cells. Figure 18.a shows the schematic of the two device configurations together with the representative J - V characteristics for the best devices, both of them processed with Bi_2S_3 absorber deposited at 450 $^{\circ}\text{C}$. It can be seen that the $\text{TiO}_2/\text{Bi}_2\text{S}_3$ cell exhibits better efficiency compared to the $\text{CdS}/\text{Bi}_2\text{S}_3$ device. A set of 5 cells (0.5 cm^2 contact area) were fabricated for each device structure, leading to an average device performance of $\eta \sim 0.1 \pm 0.05$ % (with $V_{\text{oc}} \sim 90 \pm 10$ mV, $J_{\text{sc}} \sim 3.5 \pm 0.7$ mA/cm^2 , and $FF \sim 23 \pm 0.3$ %) and $\eta \sim 0.3 \pm 0.05$ % (with $V_{\text{oc}} \sim 190 \pm 10$ mV, $J_{\text{sc}} \sim 4.6 \pm 0.8$ mA/cm^2 , and $FF \sim 32 \pm 0.3$ %) for $\text{CdS}/\text{Bi}_2\text{S}_3$ and $\text{TiO}_2/\text{Bi}_2\text{S}_3$, respectively. For the latter configuration, the highest achieved efficiency was $\eta \sim 0.45$ %, with $V_{\text{oc}} \sim 210$ mV, $J_{\text{sc}} \sim 5.7$ mA/cm^2 , and $FF \sim 38$ %. For both device configurations, processed with Bi_2S_3 at CSS substrate temperatures below 400 $^{\circ}\text{C}$, the efficiencies tend to be zero. The EQE of the best device (Figure 18.b) shows quite modest response throughout the whole wavelength interval, in correlation with the representative J - V characteristics (Figure 18.a, top). The modified EQE plot (Figure 18.c) gave a bandgap estimation of $E_g \sim 1.2$ eV for Bi_2S_3 at room temperature, in agreement with the values reported in the literature [159].

So far, these results indicate that the morphology of Bi_2S_3 has an impact on the cell performance, however, the modest $\text{TiO}_2/\text{Bi}_2\text{S}_3$ cell efficiency (which incorporates an absorber with larger and compact grains, Figure 17.d) clearly indicates that there are other factors that drastically affect the final cell performance. On the one hand, the low EQE response suggests that the carrier collection at the contacts is well reduced. Moreover, it also indicates low carrier collection close to the buffer-absorber interface (i.e., high recombination velocity at the interface and small diffusion length of the minority carriers in bulk) [223]. The last argument is also supported by the activation energy value of $E_A \sim 0.53$ eV, obtained from V_{oc} temperature dependence (Figure 18.d). This value is well below the bandgap energy, indicating that the interface recombination has a significant role in limiting the V_{oc} of these devices. On the other hand, it is well known that the conductivity type and

carrier concentration in the absorber, together with the buffer–absorber band offset also play a significant role in the formation of the heterojunction interface and resulting space charge region (SCR). The width of the SCR at the heterojunction interface depends on many factors, but among them, the carrier concentration in both the buffer and absorber layers plays a key role. The conductivity type and carrier concentration of the Bi_2S_3 absorber layers deposited on glass substrates were analyzed by the hot-point probe and Hall measurements, respectively (Figure 18.e). For the hot probe analysis, SnS thin film deposited by CSS on the same glass substrates was used as a good p-type reference [160].

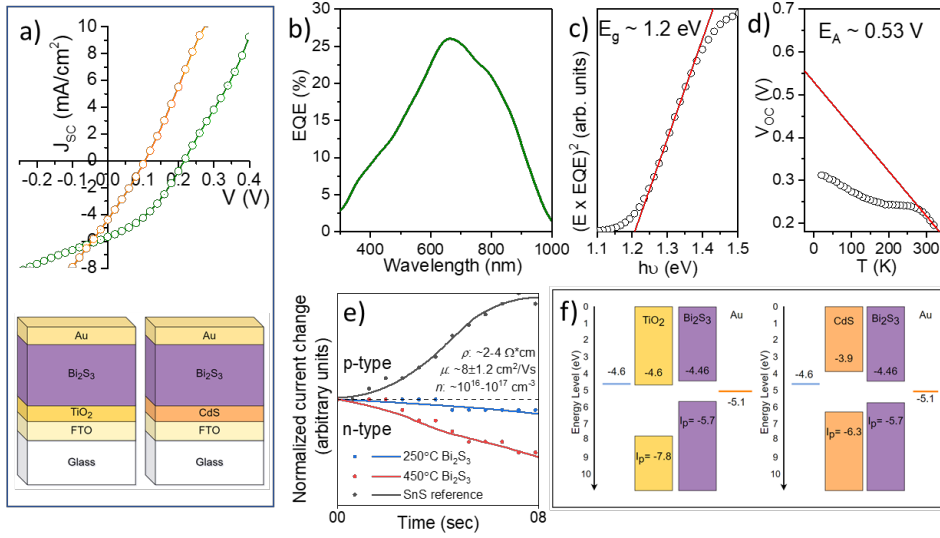


Figure 18. (a) Superstrate schematic configuration of the glass/FTO/CdS/ Bi_2S_3 /Au and glass/FTO/ TiO_2 / Bi_2S_3 /Au thin-film solar cells and representative J-V characteristics for the best devices (orange curve for CdS/ Bi_2S_3 , and green curve for TiO_2 / Bi_2S_3). (b, c) Respective EQE spectral response and related modified EQE plot, giving a bandgap estimation of 1.2 eV of Bi_2S_3 at RT. (d) V_{OC} temperature dependence together with the extrapolation to 0 K for the estimation of the activation energy (E_A). (e) hot-probe and relevant results of the Hall measurements of the carrier type and electron concentration in Bi_2S_3 thin-film absorber. (f) Band offsets with the estimation of the ionization energies for two configuration devices, measured via the photoelectron emission spectroscopy method.

Independent of the CSS deposition temperatures, the Bi_2S_3 absorber layers always showed n-type conductivity with an electron concentration of $n \sim 10^{16}$ - 10^{17} cm^{-3} and electron mobilities of $4 \pm 0.8 \text{ cm}^2/\text{V}\cdot\text{s}$ and $8 \pm 1.2 \text{ cm}^2/\text{V}\cdot\text{s}$, for Bi_2S_3 deposited at 250 °C and 450 °C, respectively. These results imply that both CdS/ Bi_2S_3 , as well as TiO_2 / Bi_2S_3 , are described as an n-n isotype heterojunction. The high values of the electron density in the absorber imply that the SCR is very narrow and most likely extends into the buffer layer, at the heterojunction interface, leading to ineffective charge separation, and high recombination rates. All these effects justify the poor performance of the CdS and TiO_2 -based devices. In the case of both n-n isotype and n-p heterojunctions, for the n-type layer, the electron density should be 1–2 orders

of magnitude above the carrier concentration in the absorber material. This would allow an efficient charge separation and transport assuming the existence of a suitable 0.2–0.4 eV conduction band spike offset between the buffer and absorber layers [225]. In addition, the n-n isotype heterojunction device will be very sensitive to the band offset and formation of the related interface defect state density. The ionization energy values for the constituent layers in the solar cell stack were obtained from photoelectron emission spectroscopy measurements. Figure 18.f shows the band energy diagrams of CdS/Bi₂S₃ and TiO₂/Bi₂S₃ solar cells with estimated values of the ionization energies. For the CdS/Bi₂S₃ device, formation of a “spikelike” band offset can be assumed, as the conduction band minimum (CBM) of the CdS buffer layer lies above the CBM of the absorber [226]. In this case, the too-positive offset of the CdS CBM (~0.5 eV) creates a potential barrier for the excited electrons in the Bi₂S₃ absorber, opposing their drift into the buffer layer and thereby drastically lowering the J_{sc} and hence, the efficiency of the device (Figure 18.a). In the case of TiO₂/Bi₂S₃ device, however, the formation of a “clifflike” offset can be distinguished (Figure 18.f) in which the CBM of the TiO₂ film lies below that of the absorber. For such a band alignment, the back-transfer carrier recombination at the main interface, in which the electrons in the TiO₂ film recombine with holes in the Bi₂S₃ absorber via interface states, is more likely. The latter phenomenon limits the built-in voltage of the heterojunction and hence the V_{oc} and efficiency of the cell.

The above solar cell results and related analysis indicate that the TiO₂/Bi₂S₃ device is described as an n-n isotype heterojunction, and among all the aforementioned limitation effects, the high electron concentration determined by the defects in the bulk of the absorber together with recombination at the main interface are the most detrimental. In this regard, temperature-dependent admittance spectroscopy can provide more insights on defect feature in Bi₂S₃ absorber. However, our attempts to perform such measurements failed, as for such a low-quality n-n type heterojunction it was difficult to detect the inflection frequency in the admittance spectrum. However, we succeeded in performing low temperature dependence spectra, as described in the following 3.1.3 subsection.

3.1.3. Unveiling defects and possible recombination in Bi₂S₃ absorber from photoluminescence analysis

To explore the existence of possible defects in Bi₂S₃, low-temperature photoluminescence (PL) spectra were measured for Bi₂S₃ absorber layers deposited onto glass, CdS/FTO/glass and TiO₂/FTO/glass stacks. There are a few reports in the literature on PL studies of Bi₂S₃ thin films deposited by physical deposition techniques. As it has been more popular to synthesize Bi₂S₃ using chemical deposition techniques, several reports employed room temperature PL analysis for Bi₂S₃ nanowires [135], nanoleafs [227], nanoparticles and complex nanostructures [228,229], as well as for the Bi₂S₃ heterojunction-based structures for photocatalytic and hydrogen productions applications [230]. Related to Bi₂S₃ films processed by physical deposition techniques, only two relatively recent studies by Haaf et al. [132] and by Jamali et al. [149] reported room temperature PL analysis. Employing confocal photoluminescence spectroscopy, Haaf et al. proved the advantages of the high-temperature deposition range for optical properties and therefore suggest, together

with the results from both surface analysis and conductivity measurements, the preparation of solar cell structures at temperatures ≥ 240 °C during Bi_2S_3 deposition. Jamali et al. performed room temperature PL analysis for $\text{Bi}_2\text{S}_3/\text{SnS}$ thin-film heterojunction-based photodetector. Therein, the authors tentatively assigned two PL emissions with bismuth vacancy (V_{Bi}) and sulfur interstitials (S_i). However, in both aforementioned studies, the PL was not performed at low temperatures, and hence, no in-depth analysis of possible defect-related transitions was discussed. Therefore, we aimed to perform a systematic analysis of low-temperature PL and temperature PL study in CSS Bi_2S_3 thin films and provide a correlation between defect features in the absorber and the performance of the solar cell device. The temperature dependence PL spectra of Bi_2S_3 deposited on glass, $\text{CdS}/\text{FTO}/\text{glass}$, and $\text{TiO}_2/\text{FTO}/\text{glass}$ stacks are presented Publication I. Figure 19.a shows the PL spectra measured at 100 K for the Bi_2S_3 deposited at 400 °C onto TiO_2/FTO substrate. For this specific configuration, the highest PL yield was obtained, and therefore, the analysis was focused on this sample, but in general, the results can be extrapolated to the whole series of investigated structures. Looking at Figure 19.a, the broad PL band indicates the presence of a high concentration of defects in the Bi_2S_3 absorber layer. The best fitting was achieved considering three bands labeled as B1 – main emission, at 1.13 eV, B2 – at lower energies, 0.86 eV, and B3 – at higher energies, 1.23 eV. To further understand the origin of these three emissions, the displacement of the band's positions depending on the measurement temperature was analyzed. Figure 19.b-d shows this dependence for all three bands and it can be observed that all the bands follow almost the same trend with increasing of the temperature, distinguishing three regions: region-(I) low-temperature region, 10-75 K, in which the band position shifts towards lower energies; region-(II) between 75 K and 100 K, where the band position does not change; and region-(III) high-temperature region, 100-150 K, in which the band position shifts towards higher energies. Such behavior in the temperature dependence of band position has been observed in other materials [231] and indicates the implication of phenomena such as band-to-impurity transition in the presence of potential fluctuations in the materials and/or transitions within deep donor-deep acceptor (DD-DA) pairs.

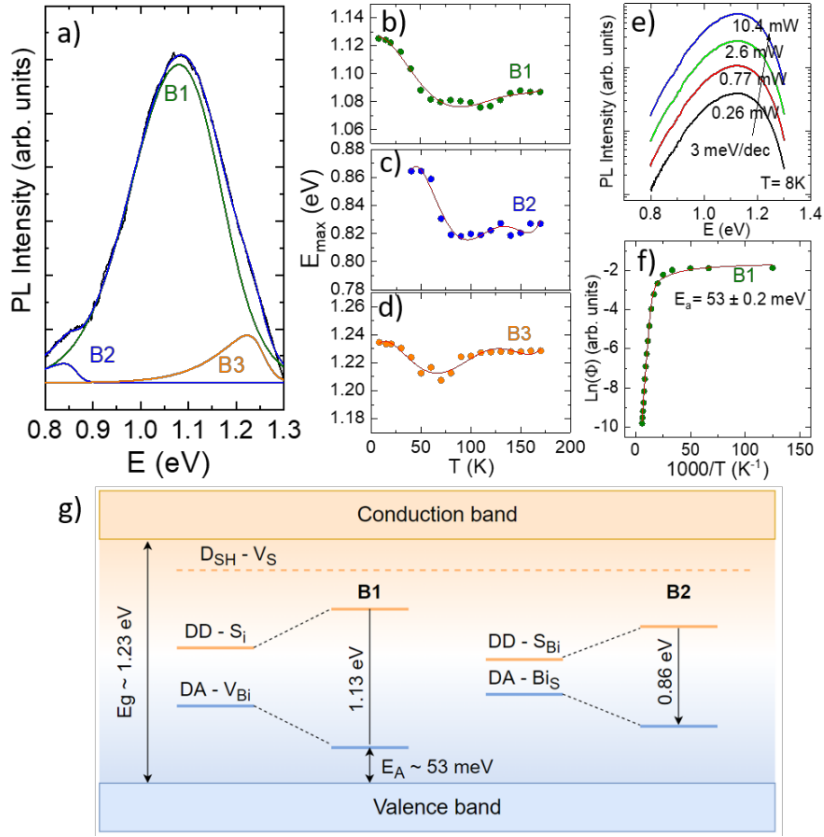


Figure 19. (a) Photoluminescence spectrum at 100 K, for Bi_2S_3 absorber layer deposited on top of $\text{TiO}_2/\text{FTO}/\text{glass}$ substrate; the best fitting was achieved with three bands: B1 at 1.13 eV (green), B2 at 0.86 eV (blue), and B3 at 1.23 eV (orange). (b-d) Shift of each band position depending on the measurement temperature. (e) Laser power dependence of the low-temperature B1 PL band, showing a shift of $\sim 3\text{ meV}$ per decade. (f) Arrhenius plots of the integral intensity of the B1 PL band with the fitting result. (g) Proposed Deep-Donor to Deep Acceptor (DD-DA) recombination model for Bi_2S_3 absorber films at 8 K. The $D_{\text{SH}} - V_{\text{S}}$ label in the diagram designates the sulfur vacancy shallow donor.

To assign one of these models, each band (B1-B3) should be analyzed separately, including additional laser power dependence measurements. For the main B1, laser power dependence (Figure 19.e) shows a very small shift of about three meV per decade. Such a small shift is possible in the case of deep DD–DA recombination. For a shallow D–A pair, a higher shift, of $\sim 10\text{ meV}$ per decade, is expected, while for the band-to-impurity transition, even a higher shift is expected, $\geq 20\text{ meV}$. The activation energy of $\sim 53 \pm 0.2\text{ meV}$ was determined from the Arrhenius plot of the resulting integral intensities for B1. Similar activation energies around 50 meV were obtained for the B1 PL band of Bi_2S_3 deposited on glass and $\text{CdS}/\text{FTO}/\text{glass}$ substrates, presented together with the respective temperature dependence PL spectra in Publication I. If to assume the implication of potential fluctuation in the material, then the activation energy should be in the range

of ~ 120 meV, so as to satisfy the correlation between bandgap energy (~ 1.2 eV) and activation energy of the respective B1-related band emission. In our case, this seems not to be the case, thus the DD–DA still remains the most probable recombination mechanism related to B1. In addition to this argument, the B1 band shape is quite symmetric, which also excludes the implications of potential fluctuation. Related to B2 emission, its broadness and small intensity suggest that it is still related to deep defects, since it is still energetically far from the bandgap energy, about 350–370 meV from the bandgap energy. Looking at the B3 emission, it has a very small intensity, and it is more prominent at higher temperatures. Considering its position at 1.23 eV, it could be related to band-to-band emission.

Coming back to the analysis of B1 emission, a natural question that arises then is how the presence of DD–DA recombination correlates with the electrical properties of Bi_2S_3 presented above. The obtained relatively high electron concentration of $10^{16} - 10^{17} \text{ cm}^{-3}$ clearly indicates the presence of shallow donors in Bi_2S_3 absorber films. A pertinent answer would be that this DD–DA involved in the B1 emission is a neutral complex that does not have an impact on the electrical properties. The initial donor is deep, and the initial acceptor is also deep, and only for the closely separated DD–DA pairs, the energy is decreasing, resulting in a rather small activation energy obtained in Figure 19.f. As a rule of thumb, this activation energy (~ 53 meV) is attributed to a shallow acceptor, as the PL temperature quenching in most of the materials is related to the acceptor level. From a theoretical perspective, the first-principles DFT calculations provide a larger variety of defects in Bi_2S_3 [159]. The donor defects, such as vacancies of sulfur (V_S), have much lower formation energies, under both, Bi-rich and S-poor or under the Bi-poor and S-rich conditions [159]. Thus, n-type conductivity and higher electron concentration is usually expected in Bi_2S_3 . Interestingly, most of the intrinsic point defects act as donors, even the anion interstitial sulfur (S_i), which is usually an acceptor in other chalcogenide semiconductors [160], acts as a donor. Only vacancies of bismuth (V_{Bi}) and antisite Bi_S act as acceptor defects [159], but both these defects are very deep (high) within the bandgap, close to the conduction band minimum, so that their ionization does not occur effectively in order to generate higher concentration hole carriers. Thus, this defect configuration makes p-type doping in Bi_2S_3 quite challenging. Based on the above PL analysis and considering the aforementioned possible formation of defects in Bi_2S_3 , a model of DD–DA recombination mechanism is proposed in Figure 19.g. For the B1 emission, the DD and DA were consistent with S_i and V_{Bi} , respectively, while the B2 band was attributed to the second DD–DA pair (next closest distance), implying a deeper donor and acceptor of S_{Bi} and Bi_S , respectively. At the same time, it is also possible that the B2 band is related to the same DD–DA pair as for the B1 band (i.e., the initial positions of defect levels will be the same), but with a larger distance between DD and DA in the lattice, resulting in slightly deeper energy levels for the DD–DA pair. Such a high concentration of defects involving a deep pair complex configuration explains why the efficiencies of the respective isotype heterojunction $\text{CdS}/\text{Bi}_2\text{S}_3$ and $\text{TiO}_2/\text{Bi}_2\text{S}_3$ solar cells are so modest.

These results are in good agreement with the first-principles theoretical predictions [159] in which the high concentration of point defects (such as Bi_S , V_S , or S_{Bi} , S_i) in Bi_2S_3 can produce deep levels in the bandgap and act as electron-hole recombination centers, decreasing the lifetime of the minority carriers and the efficiency of the solar cell. A

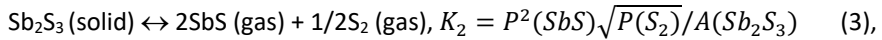
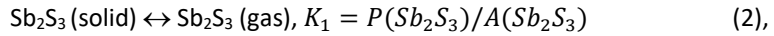
carrier lifetime on the orders of 10–50 ps [159] would be even more critical for an n-n type heterojunction with a very weak electric field. Thus, the development of p-n heterojunction Bi₂S₃ solar cells [141] can facilitate the electron-hole separation by the built-in electric field and thus increase the carrier lifetime as well as the performance of the solar cell device. Implementation of possible processing strategies, such as p-type doping of the absorber together with identification of an alternative optimal heterojunction partner layer with a suitable band offset, remains a largely unexplored approach for this material and could offer new perspectives to improve the performance of Bi₂S₃ thin-film solar cells.

3.2. (Sb_xBi_{1-x})₂S₃ solid solutions

After the study of Bi₂S₃, the next stage was the research on the (Sb_xBi_{1-x})₂S₃ solid solutions. Their development by CSS is presented in this section, covering the thermodynamic considerations for sublimation, identification of the composition-dependent growth regimes, and characterization of the structural, optoelectronic, and defect properties across the solid-solution series, providing a proof-of-concept solar cell device as well. The results presented here have been published in Publication II.

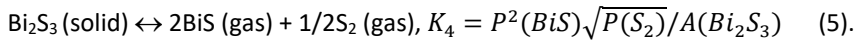
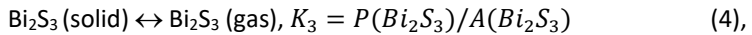
3.2.1. Thermodynamics of (Sb_xBi_{1-x})₂S₃ sublimation

Understanding the thermodynamic parameters influencing the growth of (Sb_xBi_{1-x})₂S₃ ingots and thin films is essential for optimizing their composition and phase stability during synthesis. However, to date, thermodynamic analyses of vapor-phase equilibrium and growth behavior have been largely limited to binary Sb₂S₃ [162] and Bi₂S₃ [161] systems and have not been systematically extended to composition-tunable solid-solution absorbers processed by CSS. The composition of the vapor phase can be calculated using the thermodynamic principle of minimum Gibbs energy [232,233]. The main evaporation reactions of Sb₂S₃ can be written as follows:



where all pressures (P) are expressed in atmospheres (atm), $A(\text{Sb}_2\text{S}_3)$ is activity of Sb₂S₃, and K_p are equilibrium constants of the corresponding reactions, which can be calculated using thermodynamic data of the reaction participants. Vapors of Sb₂S₃ and SbS can dissociate, causing the appearance of gaseous (SbS)₂, (SbS)₃, (SbS)₄, Sb₂S₄, Sb₃S₂, Sb₄S₃, Sb₄, Sb₃, Sb₂, and Sb.

Similar evaporation reactions of Bi₂S₃ can be written as follows:



The gaseous Bi₂S₃ and BiS can also dissociate, generating (BiS)₂, Bi₄, Bi₃, Bi₂, and Bi. Vapors of (BiS)₃, (BiS)₄, Bi₂S₄, Bi₃S₂, and Bi₄S₃ are not stable.

The constancy of Bi, Sb, and S atoms in a solid-vapor system must also be considered using the corresponding equation for pressures P :

$$\sum_i a_i P_i(\text{Bi} - \text{species}) + \sum_i b_i P_i(\text{Sb} - \text{species}) = 2/3 \sum_i c_i P_i(\text{S} - \text{species}) \quad (6),$$

where a_i (b_i , c_i) is the number of Bi (Sb, S) atoms in the Bi-related (Sb-, S-) gaseous species; the summation i is carried out over all gaseous substances. The joint calculation of equations for all K_p values (Eqs. 2-5, etc), considering constancy of Bi, Sb, and S (Eq. 6), gives the composition of vapor phase over $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions. In this case, the theory of ideal solid solutions is assumed, when the activities A of solution components (Bi_2S_3 , Sb_2S_3) are equal to their molar fractions [232]. Thermodynamic data for Sb sulfides can be found in [234], and for Bi sulfides and metal vapors can be found in [235]. Examples of such thermodynamic calculations were described in previous works [236,237].

The temperature dependences of the calculated vapor phase composition over $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid phase (where $x = 0, 0.1, 0.5$, and 0.9), calculated from the Eqs. 2-6, are shown in Figure 20. The main components of the gaseous medium over Bi_2S_3 are BiS and S_2 , with pressures of 4×10^{-10} and 2×10^{-10} atm, respectively, at 400°C . Bi_2 (4×10^{-11}) and Bi (6×10^{-11} atm at 400°C) vapors are less significant. Since the pressures of secondary gaseous substances such as Bi_2S_3 (6×10^{-17}), $(\text{BiS})_2$ (8×10^{-15}), Bi_4 (2×10^{-13}), and Bi_3 (4×10^{-15} atm at 400°C) are negligible, they are not shown.

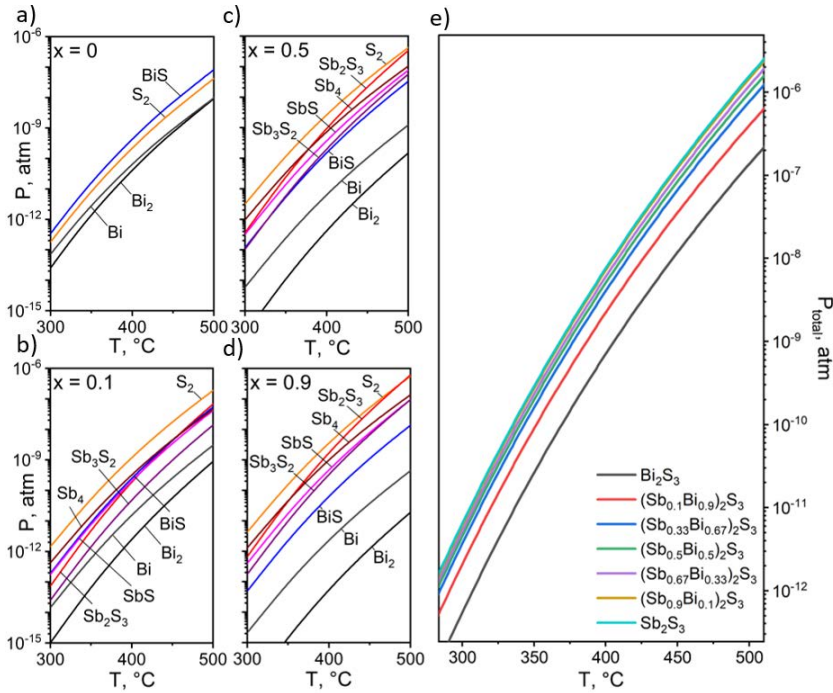


Figure 20. Thermodynamic calculations of temperature-dependent vapor composition (main components) over $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid phase in the initial evaporation stage for (a) $x = 0$ (Bi_2S_3), (b) $x = 0.1$ ($(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$), (c) $x = 0.5$ ($(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$), and (d) $x = 0.9$ ($(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$) solid phase; (e) the temperature-dependent partial pressure of the gaseous phases for different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems.

The presence of Sb_2S_3 in the solid phase causes an increase in S_2 pressure, appearance of Sb_2S_3 (1×10^{-9}), SbS (4×10^{-10}), Sb_4 (8×10^{-10}), and Sb_3S_2 (2×10^{-10} atm at 400°C and $x = 0.5$) vapors, as well as a decrease in the pressure of Bi-related species for any of the temperatures under investigation. The pressures of $(\text{SbS})_2$ (4×10^{-12}), $(\text{SbS})_3$ (3×10^{-15}), $(\text{SbS})_4$ (2×10^{-15}), Sb_2S_4 (1×10^{-11}), Sb_4S_3 (3×10^{-14}), Sb_3 (5×10^{-14}), Sb_2 (2×10^{-11}), and Sb (8×10^{-15} atm at 400°C and $x = 0.5$) are negligible; they are not shown. The calculated temperature dependences are monotonic; the total pressure increases exponentially, but the fractions of various substances are almost constant or change relatively slowly. At relatively high temperatures ($T > 500^\circ\text{C}$), Bi_2S_3 can partially dissociate to S_2 vapor and Bi-S solid phase with various activities [238]. The present calculation results correspond to the initial stage of evaporation. The calculated total pressure (P_{total}) of Sb-related species is one order of magnitude higher than that of Bi-related species ($x \sim 0.5$).

This effect is consistent with a higher volatility of Sb_2S_3 (thus, a necessity of short deposition times for Sb_2S_3 , as established in the experiment). At the same time, the surface of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ during evaporation is quickly enriched by Bi, the activity of Bi_2S_3 (Sb_2S_3) components of the system increases (decreases). The equilibrium composition of the surface should correspond to the equality: flow (Bi atoms) / flow (Sb atoms) = Bi / Sb ratio in the solid solution. This well-known effect was observed, for example, in $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ single crystal growth [239].

The influence of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid phase composition on the vapor phase in equilibrium state at various temperatures is shown in Figure 21. It can be seen that at high temperatures (at 500°C and above), an elevated content of Sb_2S_3 vapors, S_2 , and Bi-related species (mostly BiS) can be generated above the Sb-rich solid phase. The domination of Sb_2S_3 vapors above the solid Sb_2S_3 should be present at all temperatures ($300 - 600^\circ\text{C}$). At low Sb content in the solid phase ($x \leq 0.5$) and temperatures $400 - 600^\circ\text{C}$, among all the Sb-related species, SbS vapors should dominate. At the lowest temperatures (300°C), the Sb_4 vapors are expected to dominate. Thus, the thermodynamic calculation shows that the main evaporation reaction for Bi_2S_3 itself and as a part of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems is related to BiS and S_2 vapors (Eq. 5). For Sb_2S_3 it is related (i) to SbS and S_2 vapors (Eq. 3) at moderate temperatures and low Sb content in the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ system, and (ii) to Sb_2S_3 vapors (Eq. 2) at high temperatures and high Sb content.

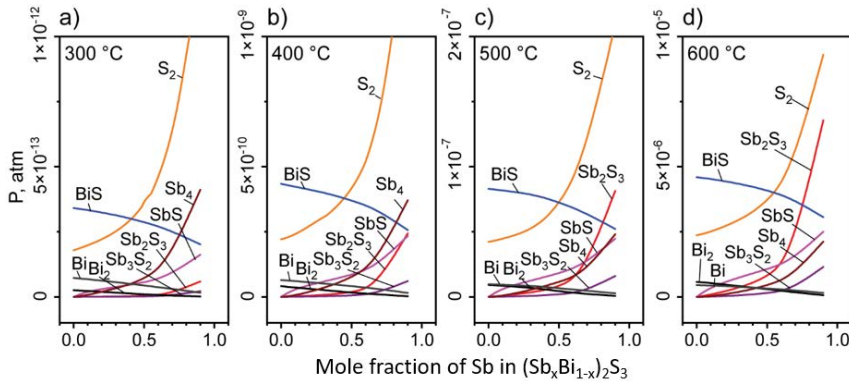


Figure 21. Influence of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ composition on the vapor pressure of different species at indicated temperatures (equilibrium state) – (a) 300°C , (b) 400°C , (c) 500°C , and (d) 600°C .

The deposition of Bi_2S_3 occurs at a relatively low vapor supersaturation (P_{total} (material source) / P_{total} (growing film)) of about 6. As shown above, in the case of low Sb content in solid phase, the main evaporation reaction for Sb_2S_3 is similar; it is related to SbS and S_2 vapors. As a consequence, the optimal growth conditions for Bi-rich systems are expected to be close to those of Bi_2S_3 . The deposition of Sb_2S_3 films occurs at relatively high vapor supersaturation (of about 10^5). Since the main evaporation reaction for Sb-rich systems is similar, being related to Sb_2S_3 vapor, the deposition of continuous and dense $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films is also expected at very high vapor supersaturation. At the same time, for intermediate values of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ composition, the film growth should be determined by intermediate values of supersaturation.

Thus, in accordance with the above thermodynamic estimation of vapor phase composition over $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, the main evaporation reaction for Bi_2S_3 and Bi-rich solid phases is based on BiS (SbS) and S_2 vapors (Eq. 3, 5), while the sublimation of Sb_2S_3 and Sb-rich solid phases occurs mostly congruently with participation of Sb_2S_3 (Eq. 2). These two evaporation mechanisms have various enthalpies, number of participated molecules, as well as molecular mass and growth rate. Three-molecular reactions (Eq. 3, 5) require slower deposition rates and consequently lower supersaturation for several molecules of the evaporation products to restructure on the substrate to form $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ crystals. The simplest one-molecular congruent evaporation (Eq. 2) does not have this limitation; the deposition of Sb-rich systems is limited mostly by re-evaporation. The parameters above (partial pressures, supersaturation values) are expected to have a significant impact on identifying the optimal CSS processing conditions for the deposition of continuous and dense films. Thus, as a next approach, the focus was set on identifying suitable CSS deposition parameters to develop continuous, uniform thin films on glass substrates.

3.2.2. Chemical composition of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions

As a first step towards the development of solid solutions and thin films, EDX analysis of the ingots of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution was performed to evaluate the effectiveness of the alloying process and ensure that the chemical composition of the ingot material aligns with the initial powder mixture. This step is critical to confirm the stoichiometric consistency and homogeneity of the source material before proceeding with thin-film fabrication via close-spaced sublimation. Figure 22.a and 22.b show the EDX results with the chemical composition of the initial Sb_2S_3 - Bi_2S_3 powder mixture and ingots, respectively. EDX analysis of the ingots (Figure 22.b) reveals that the obtained ingot alloys exhibit chemical composition and stoichiometry within a $\sim 3.5\text{at}\%$ margin from the initial Sb_2S_3 - Bi_2S_3 powder mixture, aligning well with the targeted values. Considering the above aspects on the composition of the vapor phase at various temperatures and estimated sublimation mechanisms for both Sb-rich and Bi-rich $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, it is expected that optimal CSS deposition conditions will enable the fabrication of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ films with chemical compositions closely matching those of the ingot source material. Therefore, in the next step, we systematically screened the deposition parameters – such as source temperature, substrate temperature, and deposition rate – for the growth of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ films by CSS.

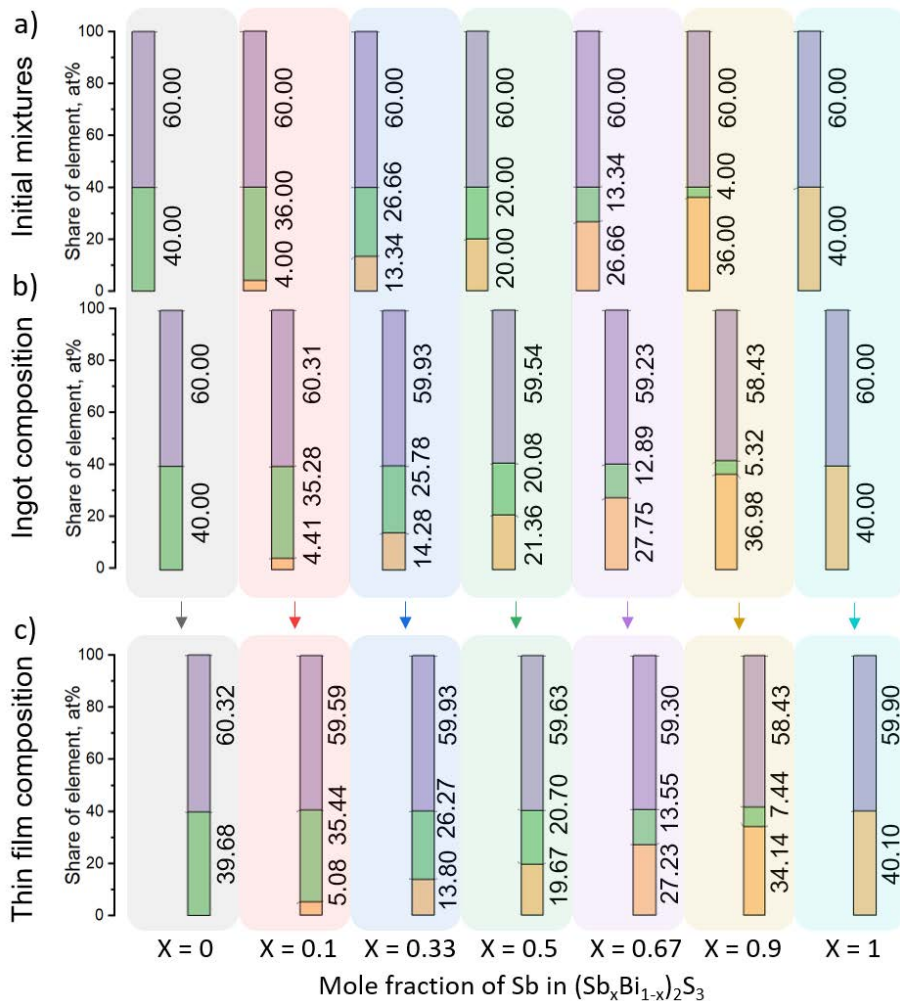


Figure 22. Elemental compositions of (a) initial Bi_2S_3 - Sb_2S_3 precursor mixtures, with given $[\text{Sb}]/[\text{Bi}]$ ratios from 0 (Bi_2S_3) to 1 (Sb_2S_3); (b) synthesized $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ ingots; (c) CSS-deposited thin films, deposited from synthesized $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ source material at the conditions given in Table 6. Orange share corresponds to Sb, green share to Bi, and violet share to S.

XRF analysis of both thin films on glass and compressed powders was conducted to complement the EDX analysis (Figure 23). $[\text{S}]$ values determined by means of XRF analyses are not reliable [240]. Therefore, only the $[\text{Sb}]:[\text{Bi}]$ ratio was measured, while $[\text{S}]$ content was suggested to be equal to the one measured by EDX.

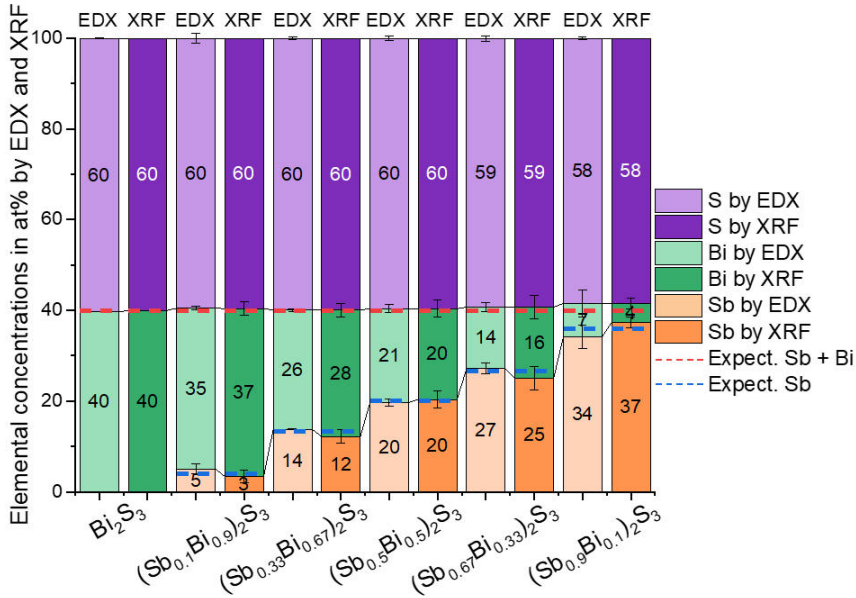


Figure 23. Chemical composition of the Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films according to (a) XRF and (b) EDX characterization.

EDX and XRF characterization provided the compatible data, showing the robustness of the selected solid solution preparation and deposition approach.

3.2.3. Composition-dependent CSS growth regimes of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films

The key target was to develop an optimized CSS processing protocol for depositing $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films with a columnar, sintered-grain morphology. As highlighted earlier, such absorber morphology is crucial for efficient charge transport in the thin-film solar cells. For this purpose, the CSS source and substrate temperatures (T_{so} , T_{sub}) were screened in a wide range, from 400 °C to 550 °C and from 250 °C to 430 °C, for T_{so} and T_{sub} , respectively. This temperature range was chosen based on the thermodynamic considerations discussed above, as well as the previously optimized CSS processing conditions for developing Sb_2S_3 [13] and Bi_2S_3 (Section 3.1). For the deposition of each $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ system (where $0.1 \leq x \leq 0.9$), the CSS deposition time was calibrated to ensure a reasonable congruent deposition rate while maintaining a consistent film thickness of $\sim 1 \mu\text{m}$. Such absorber thickness has been tested and shown to be optimal for a range of similar absorber materials (including Sb_2S_3 , Sb_2Se_3 , SnS , and Bi_2S_3) in thin-film solar cells fabricated via CSS [13,160,241]. For the Sb -rich compositions ($(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$, $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$, Sb_2S_3), a seed layer of the same material was deposited by CSS at the substrate temperature ~ 250 °C and optimized source temperature (450–500 °C) prior to the main deposition. This strategy is widely used for other similar systems, such as Sb_2S_3 and Sb_2Se_3 [13,76,241–243], especially when deposited on highly-inert substrates, such as TiO_2 ETL.

Figure 24 shows top-view and cross-sectional SEM images of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films deposited under the conditions given in Table 6. It is essential to mention that in the

figure, the SEM images are presented for the identified optimal CSS conditions of each $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ absorber layer. As shown in Figure 24, regardless of the calibrated absorber thickness (0.5 or 1 μm), optimized CSS conditions for each system resulted in conformal coating and a densely packed morphology. As expected, 1 μm -thick absorbers exhibit larger grains than 0.5 μm -thick ones. The grain size stays in the region of 0.5-1.5 μm for the 1 μm -thick films and 0.2-1 μm for the 0.5 μm -thick films. As an important result, moving from Bi-rich systems to Sb-rich ones (from left to right in Figure 24), the optimal T_{sub} decreased from 420 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$, respectively. The lowest T_{sub} of 300-320 $^{\circ}\text{C}$, enabling dense morphology for a thin film, was identified for $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$. For the latter one, the obtained T_{sub} value is in agreement with previous findings for Sb_2S_3 CSS deposition [13]. Overall, these results indicate that Sb-rich systems can be processed at relatively low temperatures, providing more options for substrate selection, including flexible and temperature-sensitive substrates.

For each of the investigated systems, any CSS deposition condition outside the optimal range in Table 6 resulted in a series of peculiarities in film morphology. It is obvious that for each system in Table 6, there is a large number of combinations between T_{so} , T_{sub} , and deposition time, which would result in various morphologies. However, for simplicity and clarity, here we highlight the observed effects in the morphology of $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ thin-film solid solutions as being representative for Bi-rich and Sb-rich systems.

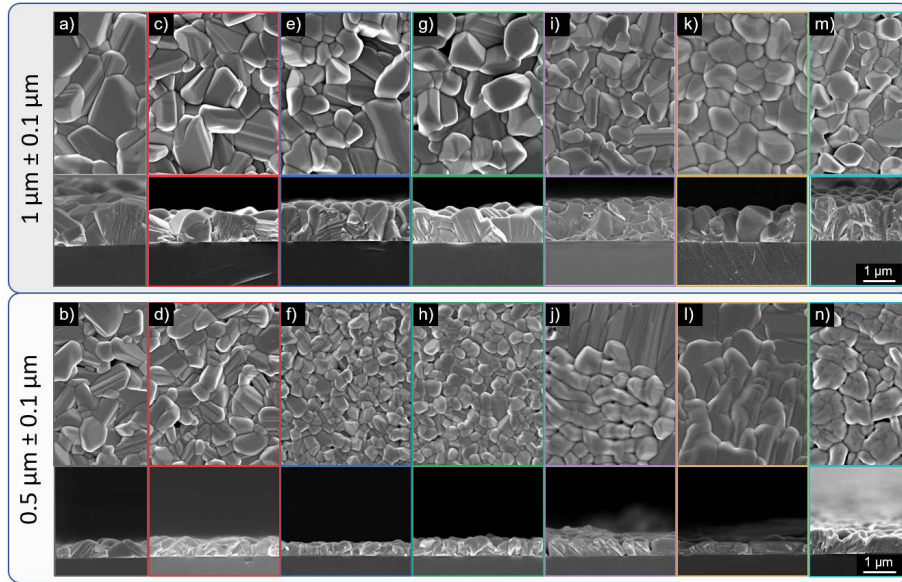


Figure 24. Top-view and cross-sectional SEM images of (a,b) Bi_2S_3 , (c,d) $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$, (e,f) $(\text{Sb}_{0.33}\text{Bi}_{0.67})_2\text{S}_3$, (g,h) $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, (i,j) $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$, (k,l) $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$, and (m,n) Sb_2S_3 thin-film absorbers deposited on glass substrate. Optimized deposition conditions for each system are summarized in Table 6. Two sets of samples are presented – with optimized CSS deposition conditions for $1 \pm 0.1 \mu\text{m}$ and $0.5 \pm 0.1 \mu\text{m}$ thick absorbers.

Table 6. Optimized deposition conditions for the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin-film absorber layers, linked to the SEM images in Figure 24. For clarity, the conditions for the series of samples calibrated to $0.5\ \mu\text{m}$ are provided. The abbreviations are defined as follows: T_{so} - source temperature, T_{sub} - substrate temperature, Log_{10} – logarithmic ratio between the supersaturation pressures above the source and substrate at given temperatures, DepRate – deposition rate.

Source material	T_{so} (°C)	T_{sub} (°C)	Log_{10} (vapor supersaturation ratio)	Deposition time (min)	DepRate (nm/min)	Need for a seed layer (Yes/No)
Bi_2S_3	460-480	410-430	0.7-1.6	40	20-50	No
$(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$	450-480	410-430	0.7-1.6	40	20-50	No
$(\text{Sb}_{0.33}\text{Bi}_{0.67})_2\text{S}_3$	460-470	380-420	0.9-2.2	30	30-70	No
$(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$	460-470	380-400	1.4-2.2	30	30-90	No
$(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$	470-480	340-360	3.3-3.6	7	50-130	Yes
$(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$	480-500	300-320	4.3-5.4	2	100-500	Yes
Sb_2S_3	490-510	280-320	4.5-6.3	1	1000-3000	Yes

Figure 25.a. shows the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ thin film deposited at T_{sub} of $300\ ^\circ\text{C}$ (which is within the optimal temperature range, see Table 6) but at lower T_{so} of $450\ ^\circ\text{C}$ for 2 minutes, implying a low deposition rate of $\sim 100\ \text{nm/min}$. As can be seen, in this case, while the film preserves the same densely packed morphology in cross-section view, the top view shows smoother grains. For the same thin-film absorber, an increase of both T_{sub} to $400\ ^\circ\text{C}$ and T_{so} to $500\ ^\circ\text{C}$ (while keeping the same deposition time of 2 minutes) leads to drastic changes in morphology (Figure 25.b). While the grains became more sintered, larger, and columnar in shape, a parallel effect has been observed, in which large cracks were formed throughout the whole film thickness. A similar effect was previously observed in Sb_2S_3 and explained through the difference in the thermal expansion coefficients (TECs) of orthorhombic Sb_2S_3 crystals [13]. For instance, it has been reported that the TEC of Sb_2S_3 in the [010] crystal direction is two to seven times larger than the TECs in the [100] and [001] crystal directions [244]. This implies that, similarly to Sb_2S_3 , Sb-rich compositions could be subject to greater residual stress during the deposition process at higher temperatures. It is well-known that any accumulation of higher tensile or compressive stress will increase the probability of the formation of cracks in the films [245]. This effect can be highly pronounced in Sb-rich systems, due to higher vapor pressure, and expected sublimation at lower temperatures. Therefore, higher substrate temperatures lead to crack formation in the films.

Similarly, analyzing the side effects for the $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ system, two distinct edge cases of deposition rate influence are depicted. Figure 25.c shows the thin film deposited at T_{sub} of $440\ ^\circ\text{C}$ (higher than the optimal range) and T_{so} of $480\ ^\circ\text{C}$ (within the optimal range). The deposition took 8 minutes, but due to the low deposition rate ($\sim 8\ \text{nm/min}$), it was not enough to fully cover the substrate, leaving multiple voids between the grains. On the opposite side, for $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ films deposited at T_{sub} of $450\ ^\circ\text{C}$ for 1 min (slightly higher than the optimal T_{sub} of $420\ ^\circ\text{C}$) and T_{so} of $550\ ^\circ\text{C}$ (significantly higher than the

optimal T_{so} of 460 °C), the deposition rate was so high, that instead of the formation of a densely-packed thin film, separate needle-like and leaf-like grains, 1-10 μm in length, were formed (Figure 25.d). Such a result is consistent with previously published observations on Bi_2S_3 growth (Section 3.1, Figure 15), which is also a typical Bi_2S_3 morphology in the case of chemically-grown thin films.

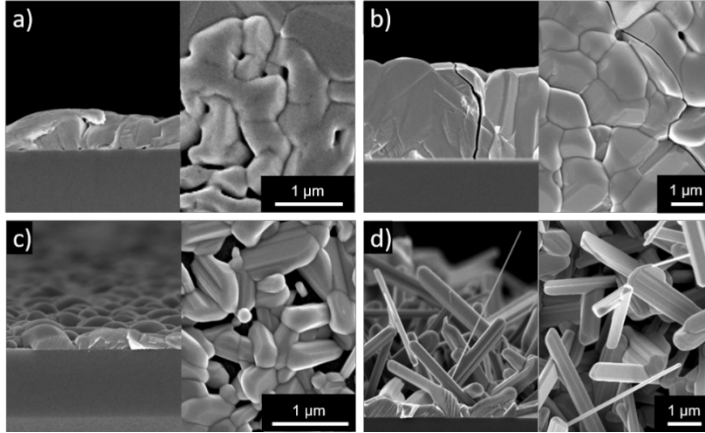


Figure 25. Top-view and cross-sectional SEM images of absorber films deposited on glass substrate for: (a) $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ thin film, deposited with the optimized T_{sub} of 300 °C and lower-than-optimal T_{so} of 450 °C, (b) $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ thin film, deposited at higher-than-optimal T_{sub} of 400 °C and optimal T_{so} of 500 °C, (c) $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$, thin film, deposited at higher-than-optimal T_{sub} of 440 °C and optimal T_{so} of 480 °C, as well as (d) $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ thin film deposited with the higher-than-optimal T_{sub} of 450 °C and higher-than-optimal T_{so} of 550 °C.

Figures 26.a and 26.b summarize the CSS deposition condition diagrams for Bi_2S_3 and Sb_2S_3 thin films, plotted as substrate temperature (T_{sub}) versus source temperature (T_{so}). These diagrams are based on our previously reported optimization studies of CSS-grown Bi_2S_3 and Sb_2S_3 thin films, and are further refined in the present work through additional parameter screening and integration into a unified growth-regime framework. Based on the systematic screening of deposition parameters described above, the investigated temperature regimes can be divided into four characteristic growth regions, reflecting different regimes governed by vapor flux, supersaturation, surface diffusion, and re-evaporation processes

In CSS, material transport from source to substrate is possible only when $T_{\text{so}} > T_{\text{sub}}$, which confines deposition to the region below the diagonal line in Figure 26; increasing T_{so} and the temperature difference $\Delta T = T_{\text{so}} - T_{\text{sub}}$ enhances vapor flux and supersaturation at the substrate surface. These general aspects, together with the thermodynamic considerations discussed in Section 3.2.1., provide a consistent framework for interpreting the experimentally observed film morphologies. We first define the optimal growth regime (OGR), which corresponds to the deposition conditions yielding dense, homogeneous thin films and serves as a reference for interpreting the remaining growth regimes (Regimes I–III). For Bi_2S_3 (Figure 26.a), the OGR is relatively

narrow and located at $T_{\text{sub}} \approx 400\text{--}430\text{ }^{\circ}\text{C}$ and $T_{\text{so}} \approx 420\text{--}480\text{ }^{\circ}\text{C}$ for glass substrates. These deposition conditions are considerably updated compared with the initial Bi_2S_3 study (Section 3.1). Notably, this optimal regime can be slightly extended toward higher T_{so} values (up to a maximum of $\sim 550\text{ }^{\circ}\text{C}$) when Bi_2S_3 is deposited on chemically and morphologically compatible substrates such as CdS or TiO_2 , as demonstrated (Section 3.1). In this regime, vapor flux, supersaturation, and surface diffusion are well balanced, enabling sufficient adatom mobility and lateral grain growth, which results in compact, densely packed films with uniform morphology.

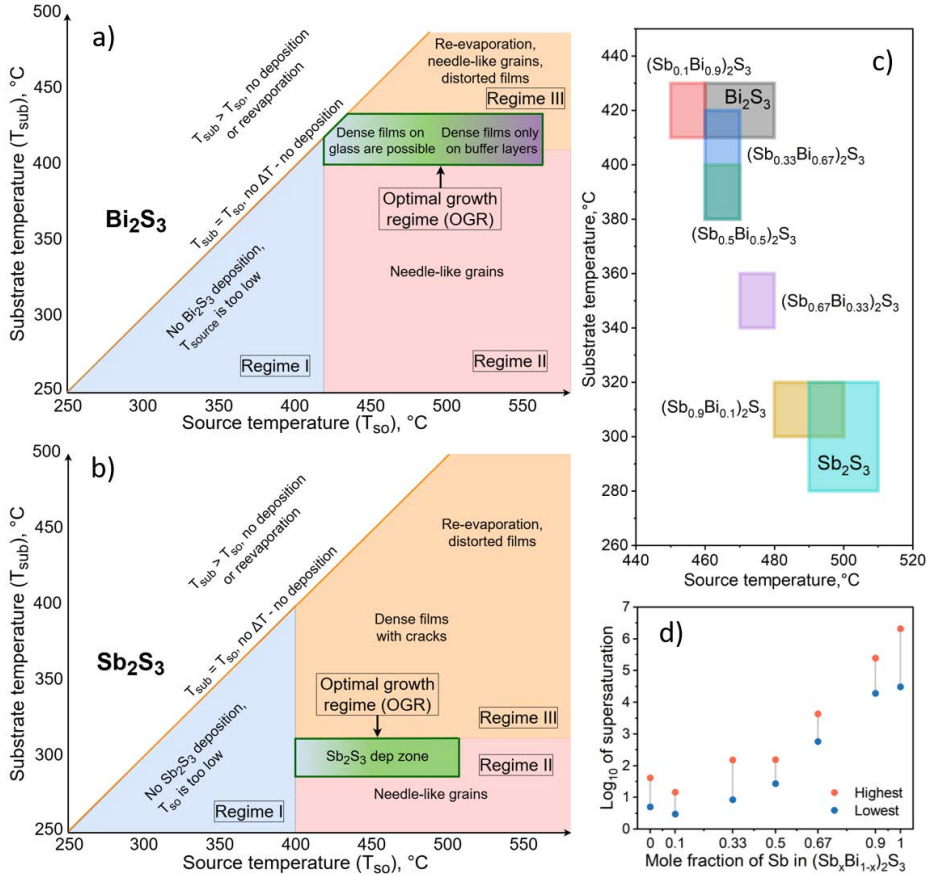


Figure 26. (a,b) Deposition conditions (T_{sub} vs T_{so}) spaces for Bi_2S_3 and Sb_2S_3 with the optimal deposition regimes (OGR, marked in green) and three suboptimal deposition regimes (Regimes 1-3); (c) the suitable temperature regions for $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems, Sb_2S_3 and Bi_2S_3 , according to Table 6; (d) $\log_{10}$ supersaturation values for the different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems.

For Sb_2S_3 (Figure 26.b), the OGR is found at $T_{\text{so}} \approx 400\text{--}510\text{ }^{\circ}\text{C}$ and $T_{\text{sub}} \approx 280\text{--}320\text{ }^{\circ}\text{C}$, exhibiting a broader tolerance toward lower substrate temperatures compared to Bi_2S_3 , in agreement with the higher volatility of Sb-containing species predicted by thermodynamic calculations (Figure 20).

Outside the OGR window, distinct sub-optimal regimes are observed. Regime I corresponds to low source temperatures, where the vapor pressure of Bi_2S_3 or Sb_2S_3 is insufficient to sustain effective material transport. In this kinetically limited regime, deposition rates are extremely low, and continuous films cannot be formed. Regime II occurs at substrate temperatures below the optimal range, where high supersaturation combined with limited surface diffusion favors kinetically driven, anisotropic growth. For both Bi_2S_3 and Sb_2S_3 , this results in the formation of needle-like or columnar structures, with feature size and density increasing with ΔT , indicating growth dominated by rapid nucleation rather than lateral grain coalescence. Regime III is observed at substrate temperatures above the OGR window, where re-evaporation of the deposited material becomes significant. Although vapor flux remains sufficient, enhanced re-evaporation at elevated substrate temperatures limits the effective surface diffusion time of adsorbed species, leading to non-homogeneous films, morphological distortion, and, in the case of Sb_2S_3 and Sb-rich alloys, an increased tendency toward film cracking.

The relevance of these growth regimes is illustrated by extending the same framework to $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films (Figure 26.c–d, Table 6). A direct comparison reveals that the optimized deposition windows for different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems are not symmetrically distributed between those of the individual compounds but are instead systematically shifted toward the Bi_2S_3 OGR, even at relatively high Sb contents. This behavior is consistent with the thermodynamic analysis in Subsection 3.2.1, which indicates that Bi-rich systems are governed predominantly by BiS/S_2 -based evaporation pathways requiring lower supersaturation, while Sb-rich systems rely increasingly on congruent Sb_2S_3 evaporation and thus demand higher supersaturation values.

This trend is further reflected in the morphology of the optimized films shown in Figure 26, where dense, conformal coatings are achieved across the entire compositional range, while the optimal T_{sub} decreases monotonically from $\sim 420^\circ\text{C}$ for Bi_2S_3 to $\sim 300^\circ\text{C}$ for Sb-rich systems. Importantly, these optimized CSS conditions yield densely packed, columnar-grained absorber layers with thicknesses of $0.5\text{--}1\ \mu\text{m}$, providing a consistent morphological basis for the comparative analysis of structural and optoelectronic properties discussed below.

3.2.4. Phase composition of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions

To confirm phase formation and assess local structural homogeneity, Raman scattering spectroscopy was performed on the CSS-deposited thin films (Figure 27). The Raman spectra of the binary Bi_2S_3 and Sb_2S_3 systems exhibit their characteristic vibrational modes, with no detectable signatures of secondary phases and relatively narrow full width at half maximum (FWHM), indicating good crystalline quality. For the solid solutions, a gradual blueshift and systematic intensity redistribution of the main Raman modes are observed with increasing Sb content, consistent with the continuous evolution of lattice dynamics in the solid-solution system and in agreement with the XRD results.

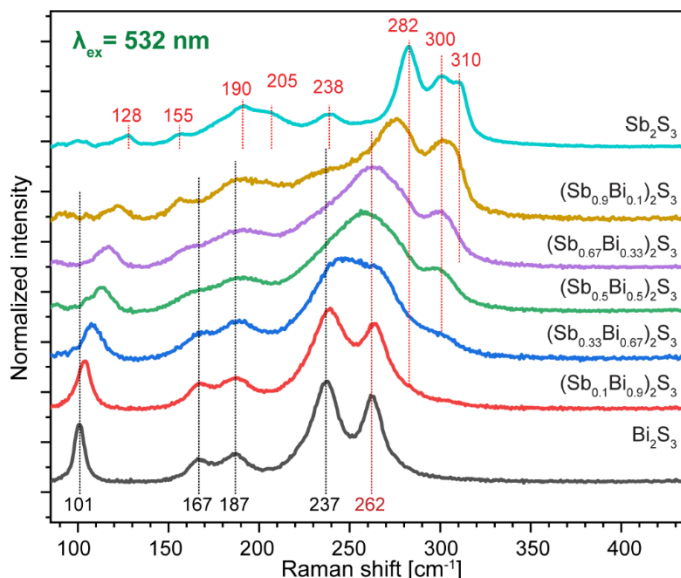


Figure 27. Raman scattering spectra of the CSS-deposited Bi_2S_3 , Sb_2S_3 , and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films with different $[\text{Sb}]/[\text{Bi}]$ ratios.

A weak Raman feature appearing at approximately 282 cm^{-1} is detected for the $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ composition and persists for all films with higher Sb content. This mode corresponds to the dominant Sb_2S_3 vibration and may indicate the presence of Sb-rich region at the film surface, coexisting with the main solid-solution phase. Additionally, an increase in FWHM is observed for compositions close to $x \approx 0.5$, indicating a reduction in crystalline order, which is a typical feature of solid solutions near equimolar composition due to enhanced configurational disorder. Overall, the combined XRD and Raman analyses confirm the successful formation of orthorhombic $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions in both powder and thin-film form across the investigated compositional range. The observed systematic lattice evolution, together with the preservation of the crystal structure and good phase homogeneity under optimized CSS conditions, provides a robust structural basis for further comparative analysis of the optoelectronic properties.

Detailed structural characterization by BBXRD, including lattice parameter evolution across the range of solid solutions, is presented in Section 3.3.

3.2.5. Composition-dependent optoelectronic properties and charge transport

With the optimized dense-film morphology and preserved crystal structure across the entire compositional range, the optoelectronic properties of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions were systematically investigated. The electrical properties of the CSS-deposited thin films were evaluated by Hall-effect measurements, and the extracted resistivity and charge carrier density are summarized in Figure 28.a and 28.b. A pronounced composition-dependent trend is observed across the solid-solution series. While Bi_2S_3 exhibits low resistivity and high electron concentration, consistent with its intrinsic n-type character, increasing Sb content leads to a strong increase in resistivity accompanied by a gradual reduction in carrier density. While the $(\text{Sb}_{0.33}\text{Bi}_{0.67})_2\text{S}_3$ is still a

predominantly n-type material, starting from $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, a p-type conductivity prevails. Overall, moving from Bi-rich compositions (e.g. Bi_2S_3 and $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$) to Sb-rich compositions (e.g. $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$), the resistivity spans a wide range from approximately $5 \text{ } \Omega\cdot\text{cm}$ to $10^6 \text{ } \Omega\cdot\text{cm}$, and carrier concentration from $\sim 10^{17} \text{ 1/cm}^3$ to $\sim 10^{11} \text{ 1/cm}^3$. For the mobility measurements, no clear trend has been observed with values between $3 \text{ cm}^2/\text{Vs}$ and $11 \text{ cm}^2/\text{Vs}$ for the entire compositional range. Such values are pertinent (and in agreement with previously reported values in similar systems, such as SnS [160]), considering the particularity of Hall measurements in the lateral direction on glass substrates. It is expected that measurements in the vertical direction (e.g. time-of-flight and carrier dynamic measurements) may provide higher values.

The incorporation of a small amount of the secondary cation does not immediately alter the electrical behavior. Both $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ exhibit transport properties comparable to those of their respective host binary systems, indicating that in the low substitution limit of the solid solution, the dominant conduction mechanism is not significantly perturbed. This behavior suggests that, at low substitution levels within the solid-solution series, the electrical properties remain largely governed by the intrinsic defect chemistry of the host binary system, whereas increasing alloying toward intermediate and Sb-rich compositions leads to a progressive modification of the electronic structure and transport characteristics.

At the microscopic level, this behavior can be tentatively rationalized by considering the evolution of defect states upon cation substitution. The observed transport behavior at low Bi incorporation levels is consistent with our recent detailed analysis of the electronic structure and defect states in Bi_2S_3 , Sb_2S_3 , and their solid solutions using energy-resolved electrochemical impedance spectroscopy (ER-EIS) [246]. Therein, it was demonstrated that pristine Sb_2S_3 exhibits pronounced deep defect states within the bandgap, which act as efficient non-radiative recombination centers and are considered a major limitation for achieving high open-circuit voltages in Sb_2S_3 -based solar cells.

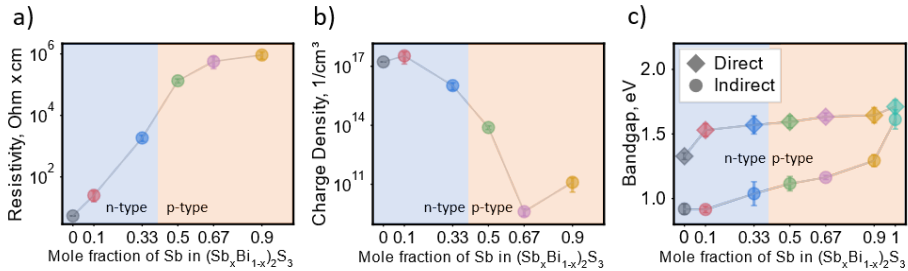


Figure 28. Composition-dependent change of the (a) resistivity, (b) charge density measured by Hall measurement, and the (c) direct and indirect transition bandgaps in $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films measured by UV-Vis. Predominant conductivity type is highlighted by the background color, blue for n-type and orange for p-type.

Notably, already a small Bi incorporation corresponding to the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ composition was shown to transform these deep defect states into shallow ones, while largely preserving the band edge positions characteristic of Sb_2S_3 . This defect “healing” effect provides a microscopic explanation for the retention of Sb_2S_3 -like transport characteristics at low

alloying levels and highlights cation substitution as a potential effective strategy to suppress mid-gap defects without fundamentally altering the host electronic structure, thereby offering a promising pathway toward improved electrical performance and, ultimately, higher device voltages.

The optical properties of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution thin films were investigated by UV–Vis absorption spectroscopy to evaluate the evolution of the bandgap values as a function of composition. All films exhibit strong absorption throughout the visible spectral range, enabling reliable extraction of optical bandgaps using Tauc analysis. The absorption edges show well-defined linear regions in both direct and indirect transition representations, indicating that both transition types may contribute to the optical response of these systems. Since a linear Tauc region can be forced for either exponent, the transition character is not established by the fit alone but is anchored by the complementary DFT and ER-EIS study [246], where the calculated band structure places the direct and indirect edges within a few hundredths of an eV of each other for Sb_2S_3 (1.45 and 1.48 eV respectively) and an orthogonal density-of-states measurement independently reproduces the gap magnitudes. A systematic and nearly monotonic widening of the optical bandgap is observed with increasing Sb content across the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution series. The direct optical bandgap increases from 1.31 ± 0.03 eV for Bi_2S_3 to 1.72 ± 0.16 eV for Sb_2S_3 , while the indirect bandgap increases from 0.88 ± 0.12 eV to 1.57 ± 0.18 eV over the same compositional range. On the one hand, the extracted direct bandgap values are in good agreement with those previously reported for solution-processed Bi_2S_3 and Sb_2S_3 thin films, indicating that the band-edge positions are largely preserved across different deposition routes [175]. On the other hand, experimental reports on indirect bandgap energies in these materials remain scarce, as indirect transitions have so far been discussed primarily based on theoretical predictions. In this context, the present absorption analysis provides experimental estimates of indirect transition energies that are consistent with theoretically predicted values [17], supporting the coexistence of direct and indirect optical transitions in this class of quasi-one-dimensional chalcogenides. For Sb_2S_3 the energy difference between the direct and indirect transitions remains relatively small ($\Delta E \approx 0.15$ eV), in line with previous experimental and theoretical studies and suggesting the presence of multiple optically active transition pathways [17]. The smooth evolution of the optical bandgap across the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution series confirms that cation substitution enables effective bandgap tunability without introducing abrupt changes in optical absorption behavior, even in the dilute substitution regime. This independent tunability of optical bandgap and electrical conductivity highlights the versatility of the system for absorber optimization, particularly in the context of PV applications where balancing light absorption, carrier extraction, and recombination losses is critical.

3.2.6. Low-temperature photoluminescence and radiative recombination pathways

To gain insight into radiative recombination processes, we next performed photoluminescence (PL) measurements. To the best of our knowledge, PL studies of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions have not been reported previously, neither at room temperature nor at low temperatures. Here, low-temperature PL is employed as a first experimental probe of radiative recombination in CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, with direct comparison to reference PL spectra of the binary Bi_2S_3 and Sb_2S_3 compounds included in Figure 29.

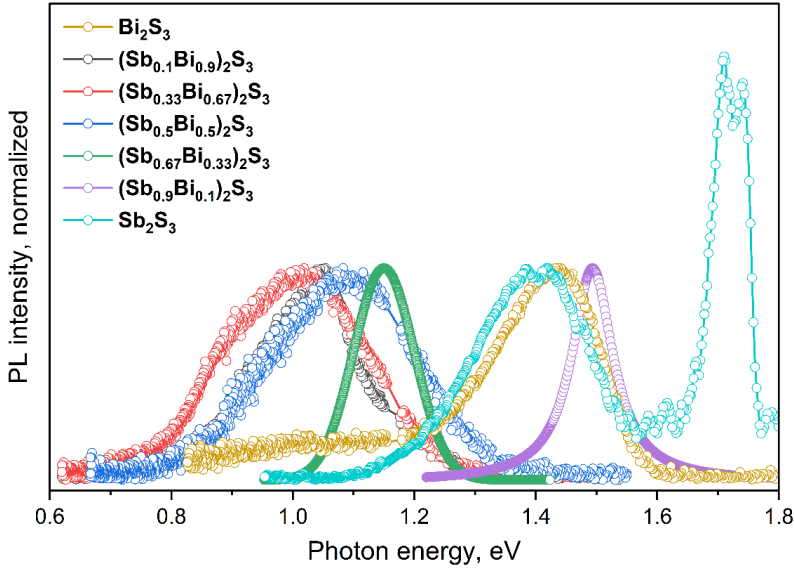


Figure 29. Low-temperature photoluminescence spectra for Sb_2S_3 , Bi_2S_3 , and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films, measured at the wavelength of 266 nm, the maximum average power of 8 mW, and a temperature of 4 K.

In Section 3.1, based on Publication I, low-temperature PL of Bi_2S_3 was characterized by broad, multi-band emissions, with the dominant band attributed to deep donor–deep acceptor (DD–DA) recombination, whereas Sb_2S_3 exhibited two distinct contributions: a narrow band-to-band emission near 1.72 eV and a broader asymmetric band around 1.40 eV, assigned to donor–acceptor pair (DAP)-type recombination [13]. These well-established reference behaviors provide a robust framework for comparative interpretation of the PL spectra of the solid-solution films. For the alloyed compositions, detectable PL emission was obtained only at low temperatures, with rapid thermal quenching observed upon increasing temperature. As a consequence, temperature- and excitation-power-dependent PL measurements – required for unambiguous identification of recombination channels – could not be performed. At the same time, across all the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution series, the PL spectra exhibit broad and asymmetric emission bands, with peak energies systematically below the optical bandgaps extracted from UV–Vis absorption. This may indicate that radiative recombination is not dominated by free band-to-band transitions, but instead involves localized electronic states, consistent with the behavior of quasi-one-dimensional chalcogenides [70,68,94,247]. For instance, similar low-temperature PL characteristics have been reported for $\text{Sb}_2(\text{S}_y\text{Se}_{1-y})_3$ solid solutions, where asymmetric emission bands were attributed to exciton-assisted and defect-related recombination accompanied by strong electron–phonon coupling [83,95], supporting the relevance of such possible mechanisms in the present system. At the same time, these PL observations are fully consistent with our recent ER-EIS analysis [246], which demonstrated that pristine Sb_2S_3 is dominated by deep mid-gap defect states, whereas already a small Bi incorporation corresponding to the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ composition leads to a transformation of deep defects into shallow states, while largely preserving the Sb_2S_3 -like band-edge positions. Within this context, the absence of

sharp band-edge PL features in the solid solutions, despite the suppression of deep mid-gap states, suggests that radiative recombination is probably governed primarily by shallow localized states and exciton-assisted processes, rather than by deep defect levels. At this stage, it is not clear whether the quasi-one-dimensional ribbon structure of the material has implications for the PL features of this material. Overall, the PL results presented here constitute a first step toward understanding radiative recombination in the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution system. Establishing a direct correlation between the defect energetics revealed by ER-EIS and the dominant radiative recombination pathways will require systematic temperature- and excitation-power-dependent PL studies, which represent an important direction for future work and will be critical for linking defect physics to device-relevant performance.

3.2.7. Proof-of-concept solar cell demonstration

Having established that $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution thin films can be reproducibly deposited with well-controlled structural and optoelectronic properties, we next assess their functionality as absorber layers in thin-film solar cells. Rather than pursuing full device optimization across all compositions, which lies beyond the scope of this study, our aim is to demonstrate a proof-of-concept photovoltaic device validating the viability of CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ absorbers. For this purpose, $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ absorber was selected based on two considerations: (i) ER-EIS analysis showed that even limited Bi incorporation transforms deep mid-gap defects into shallow states while preserving Sb_2S_3 -like band edges [246], favorable for achieving higher open-circuit voltages; and (ii) its relatively wide bandgap ($\sim 1.6\text{--}1.7$ eV) is well suited for wide-bandgap absorber applications, including tandem top cells and indoor PV.

Based on the previously identified optimal growth regime (OGR), superstrate devices with the architecture glass/FTO/CdS/ $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ /Au were fabricated without further optimization of the CSS deposition parameters. CdS was selected as an ETL due to its maturity in development and compatibility with a wide range of chalcogenide device platforms [13,160,248,249]. The absorber was deposited at $T_{\text{sub}} \sim 300$ °C and $T_{\text{so}} \sim 500$ °C for ~ 2 min, yielding compact films with thicknesses of ~ 0.8 μm . The CdS ETL was deposited under established conditions previously optimized for Bi_2S_3 - and Sb_2S_3 -based devices ([13] and Publication I). A cross-sectional SEM image and schematic of the device structure are shown in Figure 30.a–b, confirming the formation of a continuous multilayer stack. The PV performance of the proof-of-concept devices is summarized in Figure 30.c–h.

The representative current–voltage (J–V) curve (Figure 30.c) yields an open-circuit voltage (V_{oc}) of 581 mV, a short-circuit current density (J_{sc}) of 6.62 mA cm^{-2} , a fill factor (FF) of 35.6%, and a power-conversion efficiency (PCE) of 1.37%. Statistical distributions of the device parameters extracted from multiple cells are shown in Figure 30.e–h, demonstrating reasonable reproducibility despite the absence of dedicated device optimization. The preliminary assessment of the device shelf stability (kept in a plastic box under dark and air exposure, without encapsulation) shows that the cell retains the PCE values of 1.33% after 1 month, 1.26% after 3 months, and 1.17% after 6 months. This suggests a potential for high stability of the device for long-term operation.

Table 7. Reported PCEs and PV parameters for Sb_2S_3 and Bi_2S_3 -based devices with absorbers deposited by CSS.

Absorber material	Reported device architecture	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Ref.
Sb_2S_3	glass/FTO/CdS/ Sb_2S_3 /Au	700	9	45.3	2.86	[209]
Sb_2S_3	glass/FTO/CdS/ Sb_2S_3 /Au	680	11.5	48	3.80	[13]
Sb_2S_3	glass/FTO/CdS/ Sb_2S_3 /Au	743	14.12	45.6	4.78	[250]
Sb_2S_3	glass/FTO/CdS/ Sb_2S_3 /Spiro-OMeTAD/Au	739	15.65	51.8	5.81	[251]
Bi_2S_3	glass/FTO/CdS/ Bi_2S_3 /Au	90	3.5	23	0.10	Publication I
$(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$	glass/FTO/CdS/ $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ /Au	581	6.6	35.6	1.37	Publication II

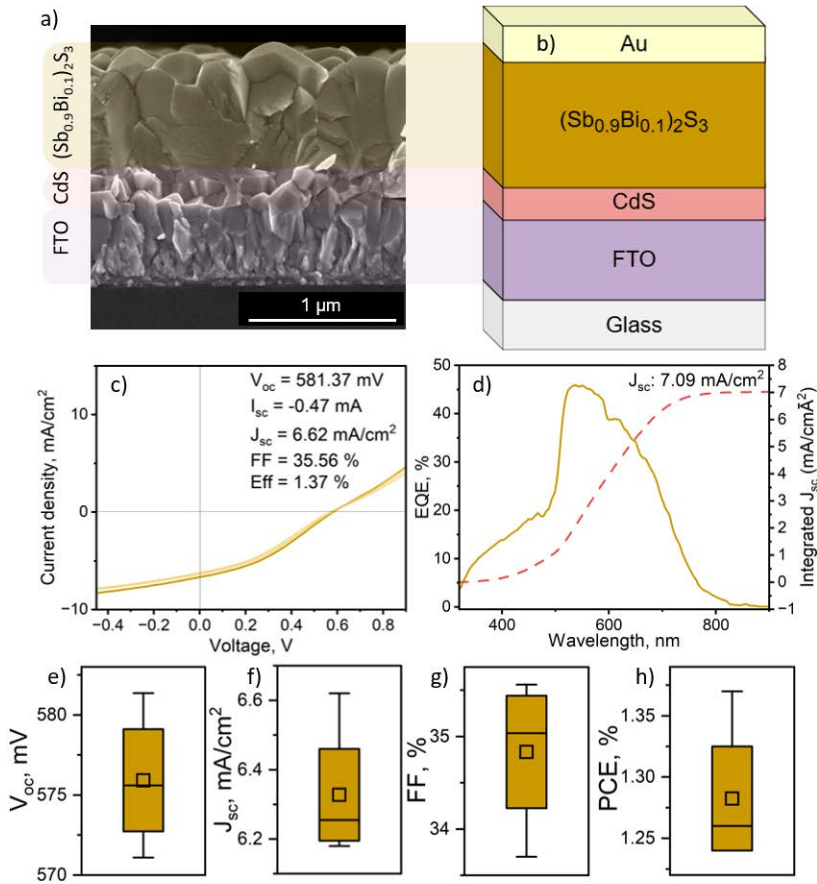


Figure 30. The $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ devices with the architecture of glass/FTO/CdS/ $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ /Au, featured on the (a) SEM cross-section image and (b) a schematic depiction, with the main photovoltaic characteristics including (c) J-V curves, (d) EQE response, (e) open circuit voltage (V_{oc}), (f) short circuit current density (J_{sc}), (g) fill factor (FF), and (h) power conversion efficiency (PCE).

At the same time, the contribution of the electrical parameters (Figure 28) to the performance of the device should not be excluded. As shown in Figures 28.a and 28.b, $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ films exhibit high resistivity ($\sim 10^6 \Omega\cdot\text{cm}$) and low carrier density of $\sim 10^{11} 1/\text{cm}^3$. This is in line with the high series resistance value of 5-8 $\text{Ohm}\cdot\text{cm}^2$, obtained for the device, implying contribution from both bulk resistance effects and non-optimal interfaces (as suggested above - presence of a rollover anomaly). On one hand, the low carrier concentration implies that the space charge region (SCR) is virtually located within the absorber, which is known to be suitable for the p-n heterojunction model [225]. On the other hand, the high resistivity (and, probably, presence of other deep defects in the absorber [246]) may limit the carrier lifetime and diffusion length, and, hence, the carrier collection in the device. Contributions from back-contact-related barriers cannot be excluded at this stage. These observations indicate that the current device performance is limited by both interface quality and deficient carrier transport due to the highly resistive absorber in a p-n heterojunction device.

Overall, this proof-of-concept study validates the PV functionality of CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution absorbers, even in the absence of device-level optimization. The encouraging performance of the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ device, together with the demonstrated bandgap, carrier density, and defect-state tunability across the solid-solution series, provides strong confidence that significantly higher efficiencies can be achieved through systematic interface engineering, absorber thickness optimization, and exploration of alternative device architectures such as n-i-p configurations [252]. So far, our results on a proof-of-concept device show promising potential; however, there is significant room for further improvement of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, including testing and validation with alternative ETLs (e.g., TiO_2 , ZnO , SnO_2) [253–257]. Beyond conventional thin-film photovoltaics, these results open opportunities for tandem, indoor PV, and other optoelectronic applications where tailored bandgap and defect control are essential.

3.3. In-depth structural analysis of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films

In Chapter 3.2, deposition-regime maps for CSS-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin-film absorbers were established, identifying the substrate/source temperature combinations required for obtaining dense, continuous, and morphologically suitable films across the composition range. Building upon this framework, the present study focuses specifically on texture evolution within these morphology-compatible growth windows. Accordingly, the objective of the current work was not to maximize RCT values alone, but rather to identify deposition conditions simultaneously providing both suitable absorber morphology and favorable nanoribbon orientation for potential PV applications. For completeness, several films deposited slightly outside the optimal morphology regions were additionally included to illustrate the interplay between morphology evolution and texture development. The results presented here have been published in Publication III.

3.3.1. In-depth texture analysis

To analyze the structural properties of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, first, the BBXRD patterns were collected for both powders and films and are presented in Figure 31. Here, the thin films with the most prominent vertical component are depicted. $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$

powders and films maintain a crystal structure with the orthorhombic $Pnma$ space group symmetry, with no secondary phases detected.

As shown in Figure 31, the XRD patterns of both powders and thin films exhibit the characteristic reflections of orthorhombic $(Sb_xBi_{1-x})_2S_3$. The main peaks at $2\theta \approx 16-18^\circ$ (201), 22° (202), and 25° (103) are present across the entire compositional range. Reflections in the 2θ regions of $28-29^\circ$ and $32-33^\circ$, corresponding to the (112) and (212) planes, are located at slightly lower angles for Bi_2S_3 compared to Sb_2S_3 . In the $(Sb_xBi_{1-x})_2S_3$ systems, these reflections are positioned between those of the two binary systems and shift nearly linearly with the [Sb]/[Bi] ratio. Such a systematic peak shift provides reasonable evidence for the formation of a predominant single-phase solid solution across the investigated compositional range ($0.1 \leq x \leq 0.9$). In most cases, a single dominant diffraction peak is observed for each reflection, indicating good phase homogeneity. However, the appearance of weak shoulders in some reflections suggests the possible presence of local compositional fluctuations or minor secondary phases with compositions deviating slightly from the nominal stoichiometry, particularly in the mid-composition range. For all the thin films deposited at the OGR conditions (Subsection 3.2.3), it was found that the crystallite size (extracted from XRD patterns using Debye-Scherrer equation) varied in a very low margin, between 70 and 100 nm. Such values are characteristic for absorbers deposited by CSS with thin film thickness 0.5-1.0 μm (Figure 26). Such a correlation between crystallite size, grain size, and film thickness was systematically observed for similar systems, like CdTe, Sb_2S_3 , Sb_2Se_3 , SnS, etc. [13,160,258], and for absorber thickness between 1 and 2 μm , the crystallite size reaches values of 160-180 nm.

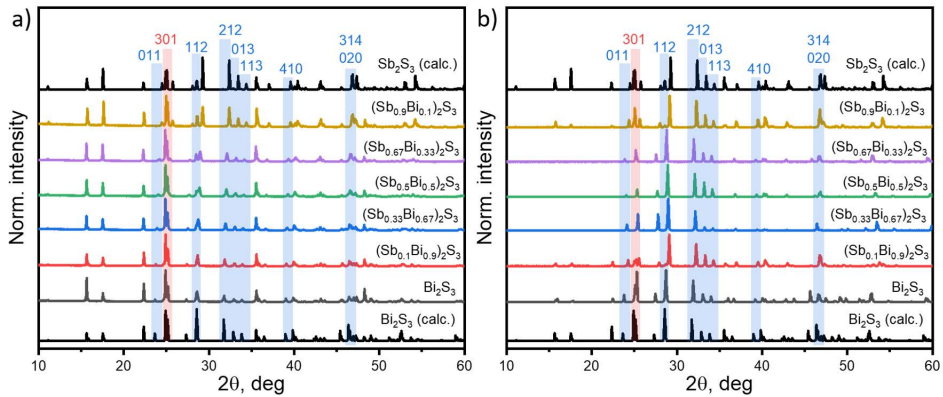


Figure 31. BBXRD patterns of $(Sb_xBi_{1-x})_2S_3$ powders (a) and thin films (b) with different [Sb]/[Bi] ratios deposited on plain soda-lime glass substrates. ICDD cards 01-083-7414 for Sb_2S_3 and 01-074-9437 for Bi_2S_3 were used to identify the reflections. The reflections corresponding to the nanoribbons parallel to the substrate are marked with red rectangles, while the ones with a vertical component are marked with blue rectangles. Calculated BBXRD patterns for the end members are given as references [167,259].

The evolution of lattice parameters extracted from the XRD data is summarized in Figure 32 for both powders and thin films. The lattice parameters a and c exhibit small variations with composition (a - from 11.24 to 11.33 Å; c - from 11.12 to 11.23 Å), whereas lattice parameter b shows a pronounced monotonic decrease from 3.98 Å for

Bi_2S_3 to 3.83 Å for Sb_2S_3 , corresponding to a contraction of ~4%. This anisotropic lattice evolution is consistent with the substitution of Bi^{3+} by the smaller Sb^{3+} cation and reflects the Q1D ribbon-like crystal structure of these compounds. Lattice parameters a and c are systematically larger in powders than in thin films, as reported in polycrystalline thin films and may be attributed to residual stress and constrained grain growth during CSS deposition [224,260]. Lattice parameter b shows negligible powder-film differences, suggesting that the lattice contraction along this direction is governed by chemical composition more than by processing-induced strain. The obtained values are in good agreement with those reported for physically-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ crystals [167], as well as for the chemically-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin-films [172,173]. However, for the physically deposited thin films, no similar data have yet been reported.

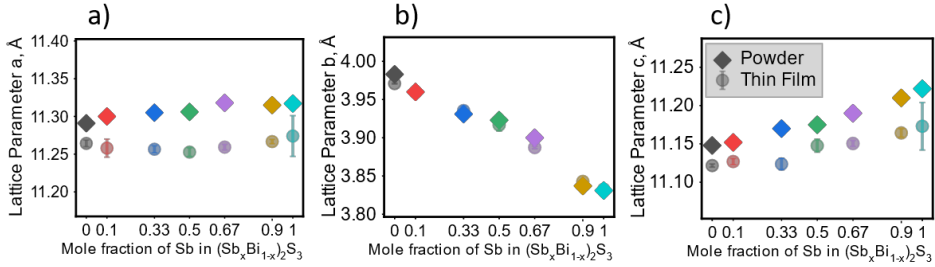


Figure 32. (a-c) Composition-dependent differences in lattice parameters for powders (diamonds) and CSS-deposited thin films (circles) of Bi_2S_3 , Sb_2S_3 , $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions (Publication II).

To learn more about the texture of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, a set of additional techniques was applied, starting from the BBXRD-based texture coefficient (TC) and ribbon carrier transport (RCT) [8,194]. Bi_2S_3 thin films, deposited at different deposition rates (measured in nm/min), are given as an example of the protocol (Figure 33.a). The same calculations were conducted for the five solid solutions $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ as well (Figure 35). TC (Figure 33.b,d) quantifies the degree of preferred orientation. Here, it is calculated according to the variation of Harris formula [78] (eq. 7), which interprets it as a percentage [219]:

$$\text{TC}(\text{hkl}) = \frac{I(\text{hkl})/I_0(\text{hkl})}{\sum_n I(\text{hkl})/I_0(\text{hkl})} \times 100\% \quad (7)$$

where the summation in the denominator is conducted for, in our case, the $n = 10$ -11 reflections, depending on the particular solid solution. Reflections were selected among the most intense ones and are highlighted in Figure 31, namely: 202, 011, 301, 103, 112, 212, 013, 113, 410, 020 (not found in $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ patterns), 314. Reflections 202, 301, and 103 correspond to the horizontal orientation of the nanoribbons, while the 020 reflection corresponds to the vertical orientation. The relation between the lattice planes corresponding to these Bragg reflections and specific angles between the normal to the substrate and the nanoribbon orientations (angle α' , terminologically following [261]) is given in Figure 33.b.

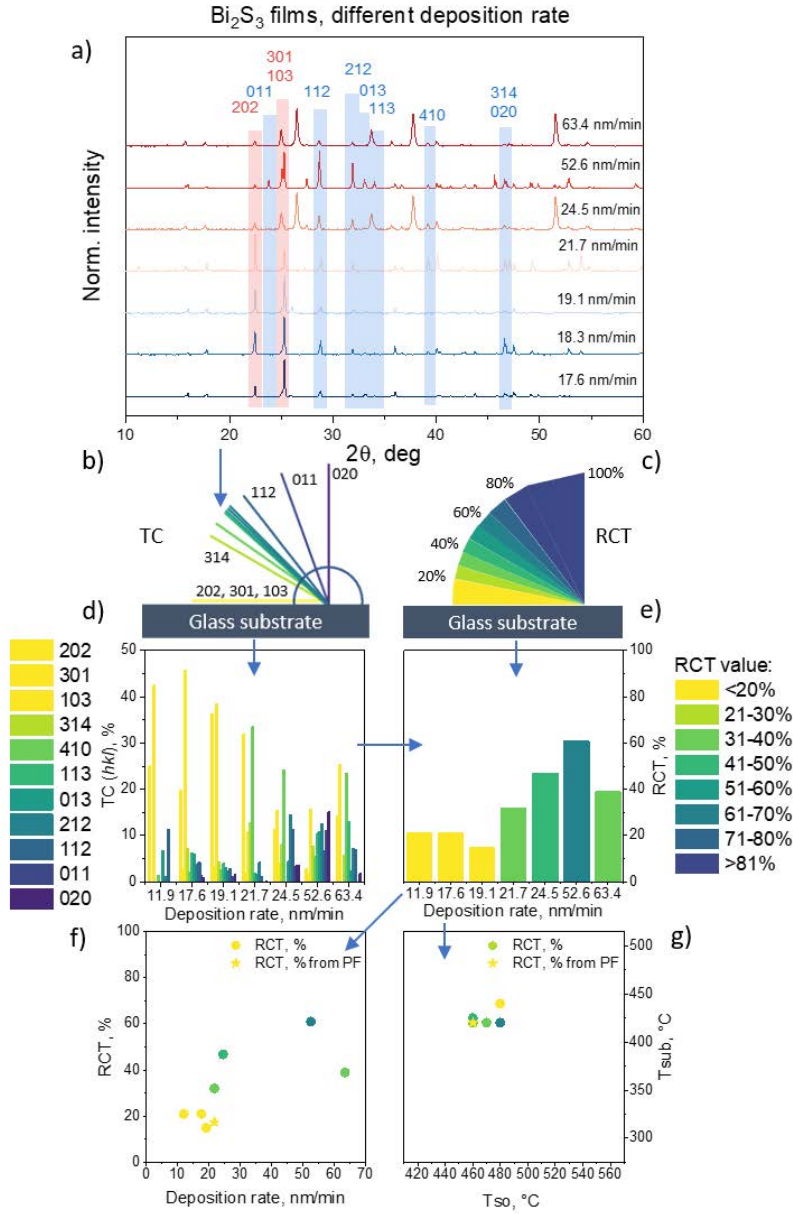


Figure 33. An example of the protocol from BBXRD data (a) to the texture information in the form of RCT. (b) Schematic diagram depicting the orientation of the nanoribbons indicated by the chosen characteristic hkl in $(Sb_xBi_{1-x})_2S_3$ solid solutions ($Pnma$ notation), (c) schematic diagram of the RCT values for different angles α' , (d) TC values for the chosen set of hkl reflections for each of the seven Bi_2S_3 samples, (e) the corresponding RCT values, (f) RCT values depicted against the deposition rate, (g) RCT values (color-coded) for the corresponding deposition conditions (T_{so} and T_{sub}).

To describe in one number the orientation of the nanoribbons in the thin film relative to the substrate, the RCT value was calculated on the basis of the TC values [194,262].

The higher the RCT value, the more favorable the nanoribbon orientation of the quasi-1D material from the PV point of view (Figure 33.c). According to Eq. 8, RCT is defined as:

$$RCT = \sum_n TC(hkl) \times EVC(hkl) \quad (8)$$

where n is the set of the selected hkl reflections, and EVC is an "effective vertical component," the cosine of the angle between the nanoribbon and the substrate normal for each hkl reflection. RCT values for the Bi_2S_3 films are given in Figure 33.e.

The RCT metric has several aspects one should consider, aiming for higher accuracy analysis:

1. It is based, by design, on a finite subset of reflections (10–11 in this work), which does not capture the full orientation distribution. In general, the reflections of the highest intensities are included in the assessment.
2. In orthorhombic materials, XRD reflections typically overlap – for example, in the Bi_2S_3 XRD pattern (ICDD 01-074-9437), the reflections 301, 103, and 111 are in close proximity at $2\theta = 24.9\text{--}25.2^\circ$, making the identification of the particular reflection less reliable. This aspect should be considered with even higher caution in solid solutions of two orthorhombic materials, since individual reflections shift at different rates across the solid solution series and each composition produces its own unique set of overlaps.
3. There is a considerable lack of specific ICDD cards for solid solutions. For the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, ICDD cards were based on the studies [167,185], and their chemical compositions did not match the ones discussed in this work. In such cases, source material powder data may be used as references.
4. RCT is unable to distinguish a multimodal (such as a bimodal vertical + horizontal) distribution from a uniform tilted distribution of similar mean angle and is insensitive to in-plane azimuthal correlation.
5. Some characteristic reflections may not be recognizable (or not be present at all) in the analyzed pattern. As an example from this work, the 020 reflection is absent from the BBXRD pattern of $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$. In such cases, other reflections with significant vertical components may provide partial sensitivity.

Nevertheless, comparison with the pole-figure-derived tilt angle α' shows agreement in the range from 0.4° to 19.8° for all the compositions where both methods were applied (Publication III), with the average and median discrepancy being 8.7° and 6.45° , respectively. The BBXRD-derived RCT is therefore used as the primary figure of merit within this study, while texture-XRD pole figures and EBSD serve as independent cross-validations.

After calculating the RCT values, it became possible to associate the verticality of the nanoribbon in the film with deposition conditions directly – namely, with deposition rate (Figure 33.f) and the source and substrate temperatures (Figure 33.g, RCT is coded by the color of the dots).

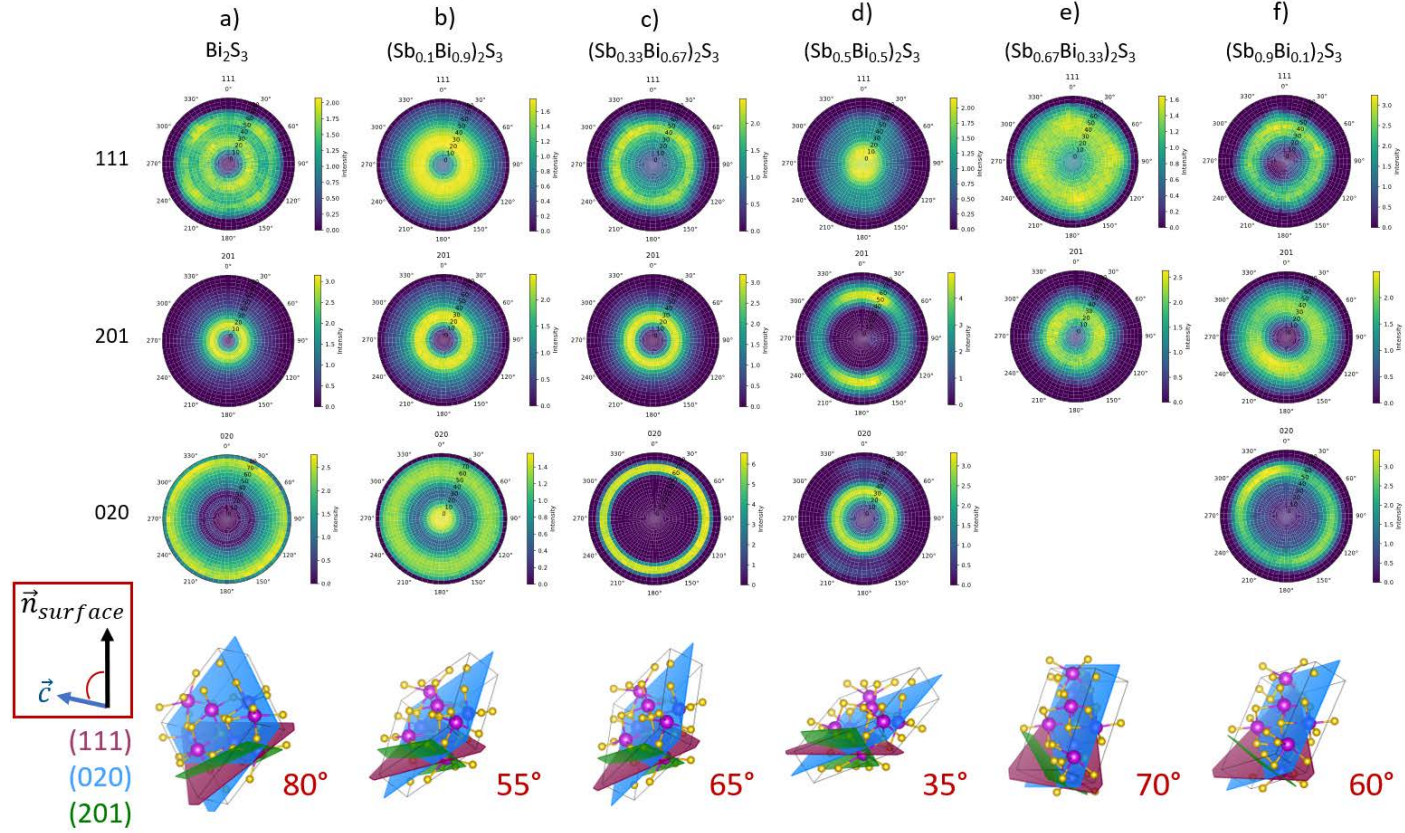


Figure 34. Pole figures of the (1) 111, (2) 201, and (3) 020 reflections of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions with (4) the resulting nanoribbon orientation (angle to substrate normal). (a – f) different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution compositions.

Texture-XRD characterization was conducted to clarify the trend in TC and RCT in $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, resulting in pole figures (PFs) in 111, 201, and 020 projections measured by XRD (Figure 34). One film was characterized for each solid solution (plus one for Bi_2S_3). Deposition conditions for the samples characterized by texture-XRD are given in the Publication III. The PFs are given with an intensity scale, which correlates directly with the multiple of random distribution. A larger multiple of random distribution corresponds to a more pronounced texture, which, in turn, translates into the preferred orientation [263]. Data were collected in the 0° – 85° χ range.

Asymmetry of the PFs for the samples $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ can be explained by the geometry of the sample - since the sample $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ was a quarter of the full circle, the sample $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ was one half of the full circle, and other samples were full circles. All the intensity maxima, obtained by the PFs, have the shape of a circle, with additional areas of high intensity at 90 degrees from each other for a 111 reflection, presumably due to the rectangular shape of the underlying substrate. For the film $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$, 020 reflection was not detected. Still, the PFs were sufficient to deduce the angles α' , given in Figure 34.4.

Having characterized the texture of individual compositions, we next compare all six systems side by side to identify composition-dependent trends. The combined outcomes of the TC, RCT, and texture-XRD analysis are given in Figure 35 for Bi_2S_3 and all five $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions. Equivalents of the RCT values from the PF analysis (Figure 34) are given in Figures 35.3–35.4 as star symbols for comparison. In Figures 35.1–35.3, TC and RCT values are given relative to the deposition rate (in nm/min) and, in Figure 35.4, relative to the deposition conditions (T_{sub} , T_{so}), as in the protocol given in Figure 33.

Each data point in Figure 35 represents an independent CSS deposition; for each composition, multiple depositions were performed across the sampled (T_{so} , T_{sub}) deposition region. The scatter within each composition is dominated by the deposition rate variation, as reflected in the strong RCT versus deposition rate correlations in Figures 35.1–35.4.

Calculated TC values for the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions thin films deposited at various deposition rates are presented in Figure 35.1. The highest deposition rate typically corresponds to the higher T_{so} and a greater difference between T_{so} and T_{sub} . At deposition rates higher than those included in this study, Bi_2S_3 and Bi-rich solid solutions, instead of densely-packed thin films, form agglomerations of randomly-oriented needle-like and leaf-like structures, while Sb_2S_3 and Sb-rich solid solutions form scale-like grains with horizontal nanoribbon orientation (Publications I and II). Due to the higher vapor pressure of Sb_2S_3 (Subsection 3.2.1), Sb-rich solid solutions have a higher deposition rate under the same deposition conditions. For Bi_2S_3 thin films (Figure 35.1.a), reflections 202, 301, and 103 (corresponding to the lateral orientation of nanoribbons) are the most prominent at a deposition rate below 20–24 nm/min, corresponding to the $T_{\text{so}} < 480^\circ\text{C}$ and $T_{\text{sub}} > 420^\circ\text{C}$ and, therefore, a ΔT below 60°C . Reflections with the higher vertical component (especially 011 and 020) are present only at a 53 nm/min deposition rate ($T_{\text{so}} = 480^\circ\text{C}$, $T_{\text{sub}} = 420^\circ\text{C}$). Surprisingly, $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ solid solution thin films (Figure 35.1.b) have the most pronounced 011 and 020 reflections among all the studied $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems, while the presence of the lateral component (202, 301, and 103 reflections) was very limited.

At the deposition rates above 180 nm/min, which correspond to $T_{\text{sub}} = 480\text{-}500\text{ }^{\circ}\text{C}$ and $T_{\text{so}} = 500\text{-}550\text{ }^{\circ}\text{C}$, especially pronounced 011 and 020 reflections were found. However, under these conditions, deposited films had uneven morphology, with the partial re-evaporation and the formation of spikes and voids instead of a dense film (Publication III). In $(\text{Sb}_{0.33}\text{Bi}_{0.67})_2\text{S}_3$ thin films (Figure 35.1.c), the most pronounced reflections were 410, 113, and 013. For $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ thin films (Figure 35.1.d), two distinct deposition rate regions were identified. For the deposition rates up to 21 nm/min ($T_{\text{so}} < 460\text{ }^{\circ}\text{C}$), the most pronounced reflections were 410, 113, and 013, while the reflections 011 and 020 were moderate. However, at deposition rates of 60-165 nm/min ($T_{\text{so}} > 460\text{ }^{\circ}\text{C}$), the reflections with a higher vertical component (011, 020) dominated, dropping again for the reference sample with $T_{\text{so}} = 550\text{ }^{\circ}\text{C}$. From Bi_2S_3 up to $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, the typical pattern was the same – stronger lateral components at lower deposition rates, stronger vertical components at higher deposition rates. For $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$ (Figure 35.1.e), increasing deposition rate corresponded to the decreasing intensity of reflections with a bigger vertical component, while the reflections 202, 301, and 314 were getting more prominent for the deposition rates above 42 nm/min ($T_{\text{so}} > 470\text{ }^{\circ}\text{C}$ and $T_{\text{sub}} = 340\text{-}350\text{ }^{\circ}\text{C}$). For $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ (Figure 35.1.f), the pattern typical for Bi-rich solid solutions was fully inverted: at the lowest applied deposition rates (128-172 nm/min, with $T_{\text{so}} = 480\text{ }^{\circ}\text{C}$ and $T_{\text{sub}} = 300\text{-}330\text{ }^{\circ}\text{C}$), the most pronounced reflections were 410 and 113, with a considerable intensity of higher vertical component reflections as well. But at the higher deposition rates ($T_{\text{so}} > 480\text{ }^{\circ}\text{C}$ and $T_{\text{sub}} = 300\text{-}380\text{ }^{\circ}\text{C}$), the lateral component overwhelmingly dominates, indicating that the nanoribbons grow mostly parallel to the substrate surface.

When comparing the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems with each other, the contribution of 020 and 011 reflections increases with the deposition rate for the Bi-rich solid solutions up to $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, and decreases for Sb-rich solid solutions. At the extremely high deposition rates (from 504 nm/min for $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ to 3351 nm/min for $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$), the higher share of Sb in the solid solution corresponded to the higher lateral and smaller vertical components.

RCT values, calculated from the TC in Figure 35.1, are given in Figure 35.2. Here, the patterns discussed in terms of the TCs are more visible. RCT values relative to a deposition rate on a linear scale are given in Figure 35.3. Cosines of the angles α' derived from the texture-XRD (Figure 34), being interpreted as %, give the same information as RCT and are shown in Figures 35.3 and 35.4 as star symbols. In most cases (with one exception of $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$), the PF-derived α' values were larger (more lateral nanoribbon orientation) than the BBXRD-derived ones (Publication III). This offset is consistent with the aspects of the BBXRD-TC-RCT pipeline in orthorhombic solid solutions, discussed above. Defocusing corrections at high χ in pole-figure measurements [264,265] may be a minor additional contributor. Overall, the PF-derived data support the texture trend observed from BBXRD.

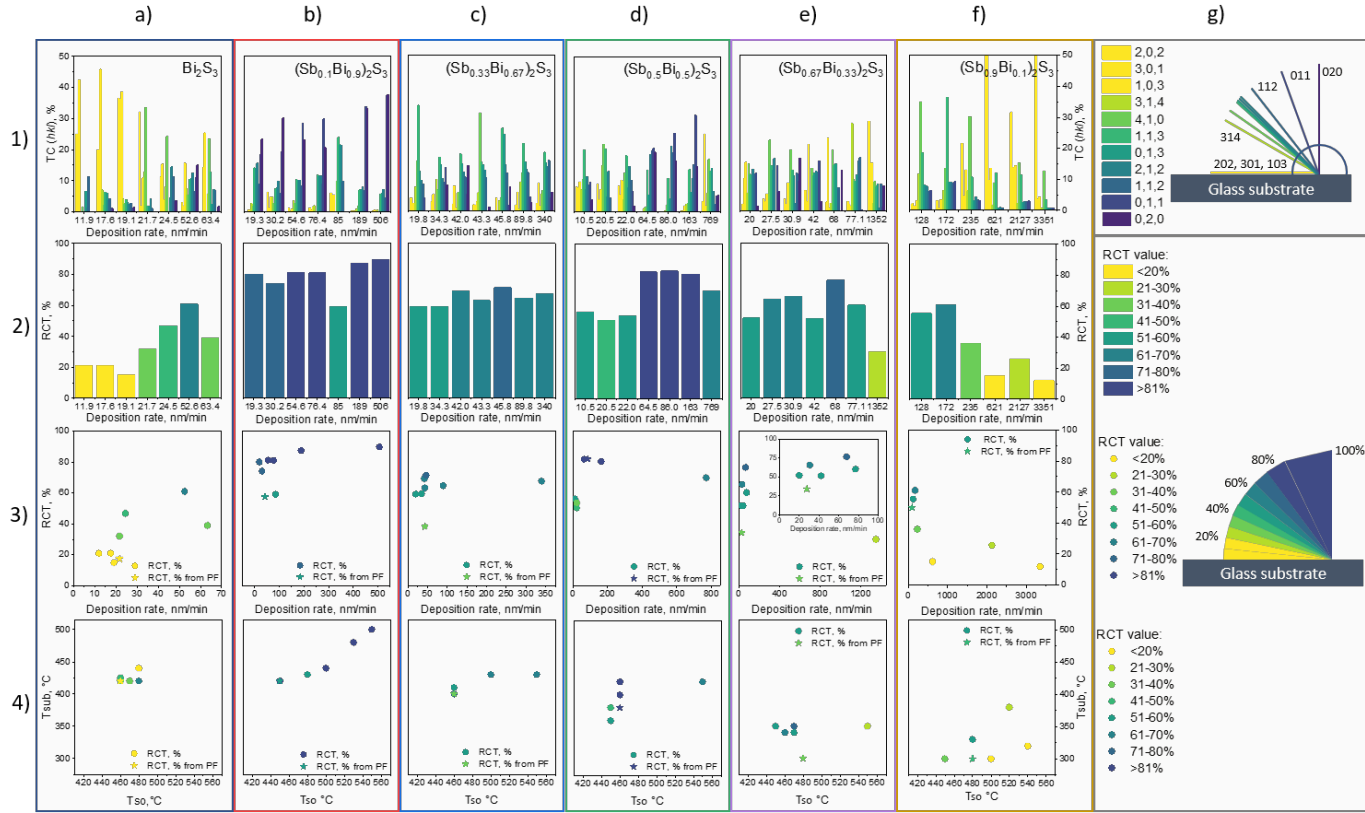


Figure 35. Rows: (1) Texture coefficients for $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films, with the reflections ordered from the ones indicating the nanoribbon growth parallel to the substrate (in yellow) to the ones indicating the nanoribbon growth perpendicular to the substrate; (2) RCT values extracted from the TC coefficients for the same samples; (3) RCT dependence on the deposition rate; (4) RCT dependence on the deposition conditions. Columns: (a – f) different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution compositions; (g) legends and visualization for TC and RCT.

The data show that Bi_2S_3 nanoribbons are lying almost parallel to the substrate at low (below 20 nm/min) deposition rates, with the highest RCT of 60.9% obtained at a 53 nm/min deposition rate ($T_{\text{so}} = 480^\circ\text{C}$, $T_{\text{sub}} = 420^\circ\text{C}$). At the same time, most $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$, $(\text{Sb}_{0.33}\text{Bi}_{0.67})_2\text{S}_3$, and $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ samples had RCT values of 55% and higher. Thus, adding 10 at% Sb_2S_3 already altered the depositional behavior of the solid solution compared to pure Bi_2S_3 . This change at only 10 at% Sb_2S_3 substitution cannot be attributed to a kinetic supersaturation shift, since $\log_{10}(\text{supersaturation})$ is essentially the same (0.7-1.6) for Bi_2S_3 and $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ (Subsection 3.2.1); the composition-driven structural origins of this observation are discussed in Subsection 3.3.2. For the growth of vertically oriented nanoribbons of $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ solid solution, the deposition rate in the region 60-160 nm/min is preferred, with an optimal rate of 86 nm/min (corresponding to $T_{\text{so}} = 460^\circ\text{C}$, $T_{\text{sub}} = 380^\circ\text{C}$), leading to the RCT value of 82.3%, while at lower deposition rates (lower T_{so} or higher T_{sub}), the films exhibit an RCT no higher than 56%. $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$ nanoribbons are generally less perpendicular to the substrate compared with more Bi-rich solid solutions, and their RCT decreases as the deposition rate increases. $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ continues the tendency, which started from $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$, with higher RCT values at lower deposition rates.

RCT values (color-coded) relative to the deposition conditions (T_{so} , T_{sub}) are given in Figure 35.4. For all the solid solutions, RCT values higher than 60% (dark-green and blue dots) were achieved via deposition in the region of $T_{\text{sub}} = 290\text{-}420^\circ\text{C}$ and $T_{\text{so}} = 450\text{-}480^\circ\text{C}$. Based on the preceding analysis, the deposition rate and conditions for the densely-packed thin films with the highest RCT values are given in Figure 36 and Table 8. The deposition conditions follow the general trend outlined in Section 3.2.

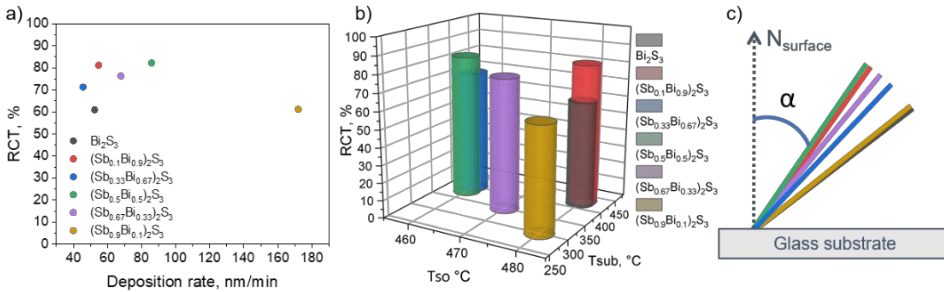


Figure 36. Deposition rates (a) and deposition conditions (b) for the CSS-deposited thin films from $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions on glass substrates with the highest RCT value, (c) visualization of the optimized nanoribbon orientations (smallest angles α') for all $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems.

The deposition conditions for the thin films with the highest BBXRD-derived RCT values (correspondingly, smallest α') among those in Figure 35, which also maintained densely-packed morphology, are given in Table 8 and Figure 36. The notable exceptions are the highly textured, but not densely-packed $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ films, deposited at higher-than-optimal T_{sub} (Publication III). The densely-packed $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ and $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ films had the highest RCT of 82.3% and 81.1%, corresponding to the smallest α' of 34.6° and 35.8° , respectively, among all the characterized samples.

Table 8. Deposition rates, T_{sub} , T_{so} , RCT, and the angles α' for the CSS-deposited thin films from $(Sb_xBi_{1-x})_2S_3$ solid solutions on glass substrates with the most vertical nanoribbon orientation.

Material	T_{so} , °C	T_{sub} , °C	DepRate, nm/min	RCT, %	Angle α' , deg.
Bi_2S_3	480	420	53	60.9	52.5
$(Sb_{0.1}Bi_{0.9})_2S_3$	480	430	55	81.1	35.8
$(Sb_{0.33}Bi_{0.67})_2S_3$	460	400	46	71.3	44.5
$(Sb_{0.5}Bi_{0.5})_2S_3$	460	380	86	82.3	34.6
$(Sb_{0.67}Bi_{0.33})_2S_3$	470	350	68	76.4	40.2
$(Sb_{0.9}Bi_{0.1})_2S_3$	480	300	172	61.2	52.3

3.3.2. On the origin of the composition-dependent texture tendencies

The composition-dependent texture evolution observed across the CSS-deposited $(Sb_xBi_{1-x})_2S_3$ series is proposed to originate from the interplay between deposition kinetics during thin-film growth/formation and the intrinsic degree of structural anisotropy of each solid solution [167]. In Section 3.2, the deposition-regime protocol for CSS-grown $(Sb_xBi_{1-x})_2S_3$ thin films was established, identifying the optimal substrate and source temperatures required for obtaining dense, continuous, and morphologically suitable films across the composition range. Within the present study, primarily thin films deposited within these morphology-compatible growth windows were selected for texture analysis.

As demonstrated by Kyono and Kimata [167], progressive substitution of Bi^{3+} by Sb^{3+} increases the stereoactivity of the ns^2 lone-pair electrons, producing increasingly distorted M-S coordination polyhedra and enhancing the bonding anisotropy of the orthorhombic stibnite–bismuthinite structure. This distortion strengthens the contrast between the strong covalent bonding along the nanoribbon axis (b -axis) and the weaker inter-ribbon interactions along the a and c directions. Consequently, the intrinsic growth-rate anisotropy progressively increases with Sb incorporation, promoting preferential elongation along the ribbon axis during crystal growth. During CSS deposition at an established optimized deposition regime (OGR), this intrinsic anisotropy interacts with supersaturation-dependent nucleation density and adatom mobility. Under moderate supersaturation and sufficiently high substrate temperatures, adatom mobility remains high enough to promote grain coalescence and competitive growth between differently oriented crystallites/nanoribbons. Under such conditions, evolution-selection mechanisms favor grains whose nanoribbon axis becomes preferentially aligned closer to the substrate normal, leading to enhanced vertical texture and higher RCT values [266].

This can be a suitable framework to explain the experimentally observed composition-dependent behavior. In Bi-rich compositions, despite relatively high substrate temperatures favorable for surface diffusion, the intrinsic growth-rate anisotropy remains comparatively weak due to the limited stereoactivity of the Bi lone pair, resulting in only modest texture evolution. Already at modest Sb incorporation, however, the enhanced lone-pair stereoactivity significantly sharpens the bonding anisotropy and strengthens orientation-selection tendencies. This effect appears particularly pronounced for $(Sb_{0.1}Bi_{0.9})_2S_3$, where only 10 at% Sb incorporation already leads to a substantial improvement in texture, yielding $RCT \approx 81.1\%$ and $\alpha' \approx 36^\circ$. Such behavior suggests that even modest Sb incorporation is sufficient to noticeably perturb the local

coordination geometry and enhance the intrinsic growth-rate anisotropy of the system. Additionally, our Raman analysis (Subsection 3.2.4) revealed a weak Sb_2S_3 -related vibrational contribution in $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$, which may indicate subtle local structural or surface-related heterogeneity additionally influencing the growth behavior. The most favorable texture is observed for $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, where the intrinsic growth anisotropy is sufficiently strong to drive preferential orientation while substrate temperatures remain high enough for effective grain coalescence and orientation evolution.

In contrast, Sb-rich compositions require substantially lower substrate temperatures and higher supersaturation conditions to maintain dense and continuous film growth (Subsection 3.2.1). Although these compositions possess intrinsically stronger structural anisotropy, the lower substrate temperatures reduce adatom mobility, while the higher supersaturation increases nucleation density. Under these kinetically constrained conditions, grain coalescence and orientation-selection processes become increasingly hindered, suppressing the development of highly vertical texture despite the stronger intrinsic anisotropy of the crystal structure.

Because all films in the present study were deposited on amorphous soda-lime glass substrates, epitaxial lattice-matching effects are not expected to play a dominant role in the observed texture evolution. Instead, the results suggest that the nanoribbon orientation is governed primarily by the interplay between composition-dependent crystal-chemical anisotropy and deposition kinetics during CSS thin-film growth.

3.3.3. EBSD cross-evaluation of the RCT and Texture-XRD findings

To independently verify the findings derived from BBXRD and texture-XRD, and to resolve the texture information at the level of individual grains, EBSD orientation mapping was conducted for the samples, which were previously examined through BBXRD (with calculation of TC and RCT) and texture-XRD. The cross-sectional EBSD maps of four samples (Bi_2S_3 , $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$, $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$) are shown in Figure 37.a-d. The observed $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ grains are larger than those of $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$. It is evident that the nanoribbon orientation in the Bi_2S_3 thin films is mostly parallel to the substrate surface, and that in $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ thin films there is a significant variety of the nanoribbon orientations among the grains, which makes it harder to discuss the preferred orientation and explains the especially dispersed PFs (see Figure 34.b,f). However, the $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ thin film exhibits a profound preferential vertical nanoribbon orientation and consists of the densely-packed columnar grains. It is in agreement with BBXRD-derived RCT and PF-derived RCT (Table 9), with all three methods showing the angles α' with an agreement of 1.4–8.7 degrees.

Table 9. Outcomes of the three different ways to assess the angles between the nanoribbon and the substrate normal (BBXRD, PF, EBSD).

Sample	BBXRD-derived		PF-derived		EBSD-derived	
	Angle α' , deg.	RCT, %	Angle α' , deg.	RCT, %	Angle α' , deg.	RCT, %
Bi_2S_3	71.33	32.00	80.00	17.36	74.00	27.56
$(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$	50.80	63.20	55.00	57.36	NaN	NaN
$(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$	34.60	82.30	35.00	81.91	36.00	80.90
$(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$	62.50	46.44	60.00	50.00	NaN	NaN

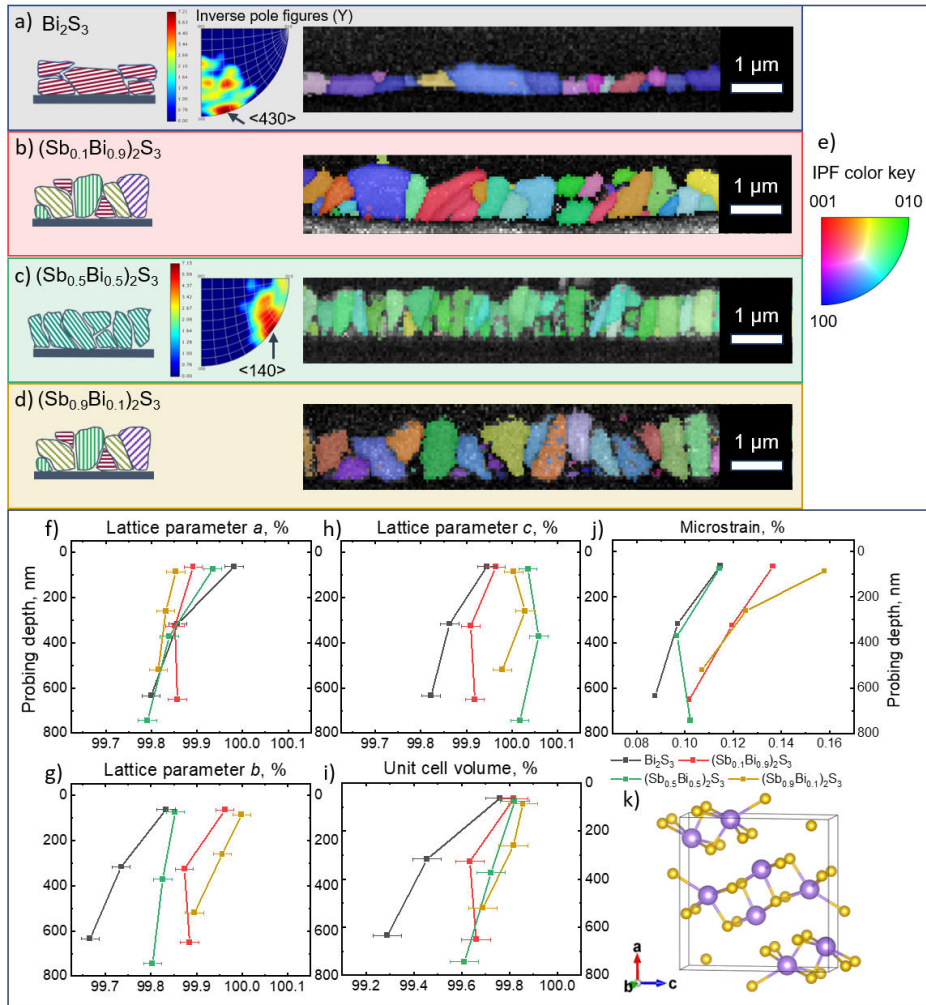


Figure 37. Texture-structure relations in CSS-deposited $(Sb_xBi_{1-x})_2S_3$ thin films. (a-d) Texture information for four thin films with the (a) most lateral, (c) most vertical and (b,d) disordered orientation of nanoribbons among the grains, including the inverse pole figures (IPF) for Y axis (the colors representing the multiples of random distribution) and EBSD cross-sections, with (e) an IPF color key; (f-i) relative change in lattice parameters and $V_{unit\ cell}$, (j) change in microstrain, and (k) a schematic depiction of a $(Sb_xBi_{1-x})_2S_3$ unit cell with corresponding vectors in $Pnma$ notation.

3.3.4. Structural depth profiling (GIXRD)

While the preceding analysis addressed the preferential orientation of nanoribbons in the films, a complementary question concerns the evolution of the crystal structure itself – specifically, whether the lattice parameters and microstrain vary through the film thickness. To address this, GIXRD depth profiling was conducted, focusing on three probing zones of the film (<65–85 nm, <240–370 nm, and <475–750 nm). One sample from each $(Sb_xBi_{1-x})_2S_3$ system was characterized, using the same samples that were also characterized by texture-XRD (deposition conditions are given in Table S2), with similar thickness and compatible roughness (Figure 23).

The main information extracted from the GIXRD data included the change in lattice parameters, and, consequently, the unit cell volume ($V_{\text{unit cell}}$), as well as the microstrain through depth of the thin film [267] (three characterized probing zones). Since all compositions share the same space group and have similar diffraction patterns, Le Bail fitting biases are expected to be systematic and largely uniform across the dataset, and are therefore unlikely to account for the composition-dependent ordering of Δa , Δb , and Δc reported in Table 10. The microstrain was determined using the Stokes-Wilson equation, with integral peak breadths (corrected for the instrumental broadening using the Thompson-Cox-Hastings pseudo-Voigt function) used as peak width parameter [268,269]. The comparison among the six analyzed thin films is shown in Figure 38. Lattice parameters and $V_{\text{unit cell}}$ are both compared as absolute values (Figure 38.a-d) and as a percentage of the reference (powder samples of the corresponding solid solutions) (Figure 38.e-h).

To assess the probability of the depth-related changes in chemical composition as the reason for the structural changes, the EDX mapping was conducted for the same samples as EBSD (Publication III). In samples $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$, the anomalies in chemical composition were indeed found:

- In the $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ sample, a layer of slightly Sb-rich and Bi-poor composition was found at the surface of the film;
- In the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ sample, a region with Sb-rich and S-poor composition was found near the substrate of the film.

At the same time, the chemical composition profiling of the samples Bi_2S_3 and $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ revealed no compositional gradients or anomalies, despite the similar changes in lattice parameters and microstrain. Therefore, the chemical composition could not be recognized as the sole reason for the detected depth-related structure changes.

Because b spans 4.3% across the full solid-solution series while a and c change by less than 1% [167], the absolute values in Figure 38.b cleanly separate the six compositions but obscure the depth-dependent signal within each. The relative representation (Figure 38.e-h), normalized to the powder reference of each composition, filters out this composition baseline and reveals the depth-dependent strain on a common scale.

On this scale, the depth-dependent variation of individual lattice parameters correlates with texture (Figure 37, Table 9): in the three films where b is not perpendicular to the substrate – Bi_2S_3 (horizontal texture), $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$, and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ (no texture) – b shows the largest or co-largest relative depth variation. In the vertically textured $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, where b is oriented normal to the substrate and therefore unconstrained, a – the inter-ribbon direction, now in-plane – takes over as the parameter with the largest depth-related variation. At the same time, the highest degree of microstrain aggregation from substrate to surface (Figure 38.i) was found in the $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ films with no texture, and in the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ film, it aggregates more than in $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$. This correlation between depth-dependent lattice parameter changes and nanoribbon orientation may reflect residual stress at the film–substrate interface, though the present GIXRD data do not allow direct stress quantification, and other contributions cannot be excluded.

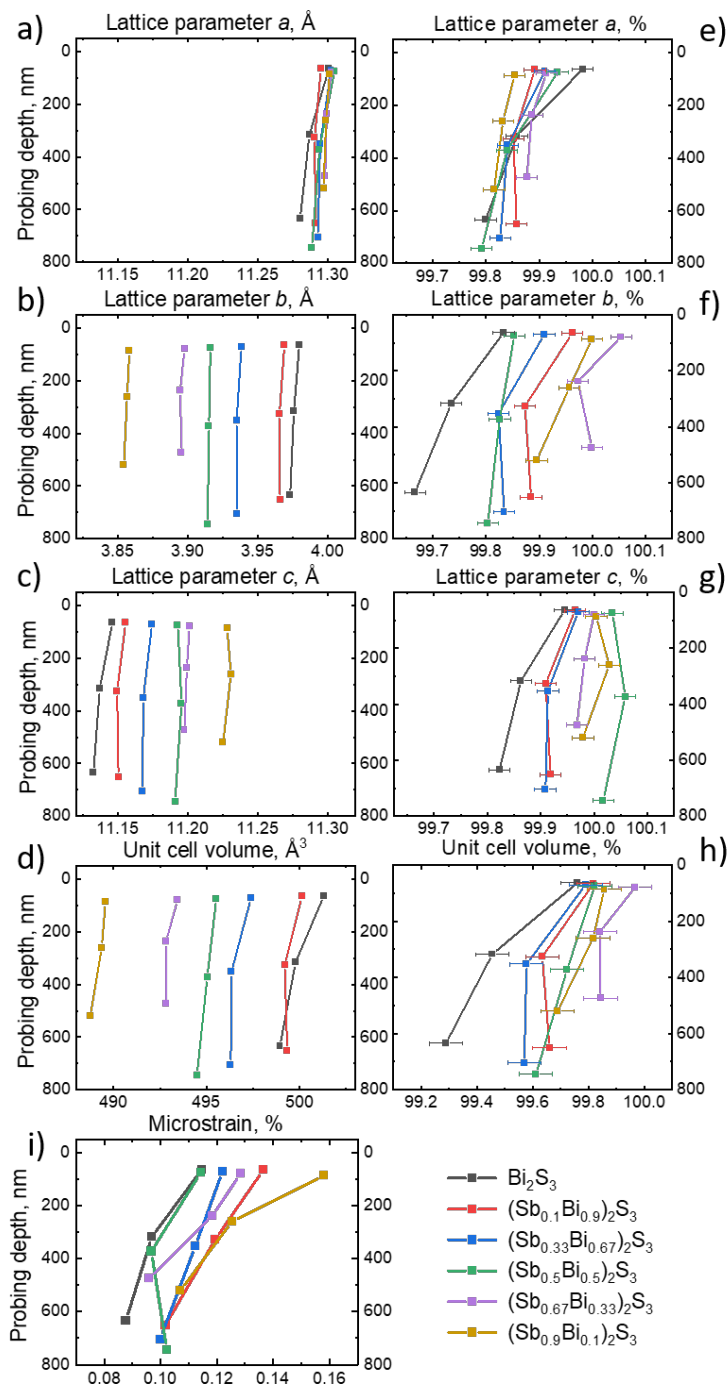


Figure 38. Change in lattice parameters, unit cell volume, and microstrain in CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, given against the probing depth. Lattice parameters and unit cell volume are given in (a-d) absolute values and (e-h) relative to the powder reference values, while (i) microstrain is always quantified in percent.

Another reason for such changes in unit cell parameters may be differences in the growth processes for vertically and horizontally oriented nanoribbons. Vertically oriented nanoribbons are limited in their growth – they must grow upward, with only rotation along the long axis [270] and some nanoribbon bending [271] as possible deviations, which may limit the possible changes in lattice parameters as well. In the case of the horizontally-oriented nanoribbons, they have at least one additional "degree of freedom": nanoribbons, deposited atop each other, may show a behavior similar to turbostratic disorder in 2D materials. For graphene [272] and MoS₂ [273], it leads to a slight increase in interlayer distances, and for quasi-one-dimensional materials, such as (Sb_xBi_{1-x})₂S₃, it may have a similar effect. Still, more research is needed in this particular area to draw stronger conclusions.

Table 10. Difference between the biggest and the smallest value among the GIXRD-derived lattice parameters, $V_{unit\ cell}$, and microstrain for the four CSS-deposited (Sb_xBi_{1-x})₂S₃ thin films for which EBSD texture assessment was available, with the biggest differences highlighted in bold.

	Texture	Δa , %	Δb , %	Δc , %	ΔV , %	$\Delta MicSt$, %
Bi_2S_3	horizontal	0.0018	0.0017	0.0012	0.0047	0.0270
$(Sb_{0.1}Bi_{0.9})_2S_3$	none	0.0003	0.0009	0.0005	0.0018	0.0345
$(Sb_{0.5}Bi_{0.5})_2S_3$	vertical	0.0014	0.0005	0.0004	0.0021	0.0176
$(Sb_{0.9}Bi_{0.1})_2S_3$	none	0.0004	0.0010	0.0005	0.0017	0.0509

Overall, this study provides a platform for future research on the structure-related deposition of (Sb_xBi_{1-x})₂S₃ thin films by physical techniques. For each solid solution, a texture baseline was established, which may be further improved by optimizing deposition conditions, introducing post-deposition procedures, or using other substrates/ETLs that may promote particular nanoribbon growth directions. While (Sb_{0.5}Bi_{0.5})₂S₃ and more Sb-rich materials are p-type and may be used with classic ETLs such as TiO₂ and CdS, Bi-rich materials, being n-type, provide additional challenges in band alignment engineering. Beyond the thin-film solar cells research, the BBXRD-TC-RCT texture analysis methodology and its cross-check by texture-XRD and EBSD, implemented in this study, may be found useful in the broader application range, including photocatalysis and other optoelectronic applications.

Conclusions

This doctoral research summarizes the development and characterization of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin-film absorbers deposited by CSS, including studies of morphology, optoelectronic properties, structure and texture, and their correlation with the CSS deposition conditions. The technological methodology for preparing Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films by CSS was successfully developed and refined to achieve better nanoribbon orientation, a crucial factor for efficient PV devices.

The main highlights from the thesis are the following:

1. CSS deposition conditions for Bi_2S_3 were optimized progressively across the publications I-II, reaching the optimal regime for glass substrate at $T_{\text{so}} = 480^\circ\text{C}$ and $T_{\text{sub}} = 420^\circ\text{C}$ and a deposition rate of 50-60 nm/min, leading to the homogeneous, dense thin films with the most vertical nanoribbons having α' of 52° . At higher ΔT , films usually had a suboptimal morphology with separate needle-like or leaf-like grains. At lower deposition rates, the nanoribbons used to lie more horizontally (bigger angle α'). For functional PV substrates such as glass/FTO/CdS and glass/FTO/ TiO_2 , much higher deposition rates were achieved for dense film fabrication compared with plain glass.
2. At all CSS deposition conditions, Bi_2S_3 thin films maintained n-type conductivity, electron concentration of $\sim 10^{16}\text{-}10^{17}\text{ cm}^{-3}$, and electron mobilities of $4.0\text{-}8.0 \pm 1.2\text{ cm}^2/\text{V}\cdot\text{s}$. Proof-of-concept CdS/ Bi_2S_3 and $\text{TiO}_2/\text{Bi}_2\text{S}_3$ superstrate PV devices had PCEs of $0.1 \pm 0.05\%$ and $0.3 \pm 0.05\%$, respectively. Low efficiencies may be attributed to deep defects in Bi_2S_3 and the n-n isotype heterojunction.
3. Low-temperature PL revealed three emission bands in Bi_2S_3 : B1 at 1.13 eV, B2 at 0.86 eV, and B3 at 1.23 eV, and a Deep Donor to Deep Acceptor (DD-DA) recombination model was proposed, consistent with the weak built-in electric field and limited carrier collection in n-n devices.
4. $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions ($x = 0, 0.1, 0.33, 0.5, 0.67, \text{ and } 0.9$) were synthesized and deposited by CSS on glass, combining thermodynamically guided screening with experimental optimization of deposition conditions for each solid solution, enabling the reproducible formation of dense, homogeneous absorber layers. The chemical composition of solid solutions and thin films stayed within 3.5 at% of the planned $[\text{Sb}]:[\text{Bi}]:[\text{S}]$ atomic ratios. Structural characterization confirms the formation of single-phase orthorhombic solid solutions.
5. Both direct and indirect bandgaps were observed in most of the solid solutions, with indirect behavior being more pronounced in Bi-rich ones, while direct behavior was more widespread among the Sb-rich ones. Between Bi_2S_3 and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$, the direct bandgap semi-linearly changed from 1.3 to 1.7 eV, and the indirect bandgap – from 0.9 to 1.25 eV, while carrier densities varied over more than two orders of magnitude. Low-temperature PL measurements, reported here for the first time for CSS-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ films, suggest radiative recombination involving localized and exciton-assisted processes.
6. A proof-of-concept superstrate CdS/ $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ solar cell achieved a PCE of 1.37% with $V_{\text{OC}} = 581\text{ mV}$, $J_{\text{SC}} = 6.62\text{ mA}/\text{cm}^2$, $\text{FF} = 35.6\%$, making it the first physically deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin-film solar cell.

7. For each $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution, trends in nanoribbon orientation were researched individually, finding the optimal deposition conditions leading to the most vertically-oriented nanoribbons. Optimal T_{so} was in the region of 460-480 °C, while the optimized T_{sub} was in the range from 420-430 °C for (Bi-rich) to 300 °C (Sb-rich). In the films with the most vertical texture, nanoribbons were oriented at 34.6 °- 52.5 ° relative to the substrate normal, with the best texture (34.6°) found in $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ thin film. The composition-dependent texture evolution was attributed to the interplay between the deposition kinetics and the Sb lone-pair stereoactivity in $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions.
8. Texture was characterized by BBXRD-derived analytical approaches (TC, RCT), texture XRD, and EBSD, providing a robust and reproducible texture analysis pipeline.
9. GIXRD depth profiling revealed that the depth-dependent evolution of lattice parameters and microstrain correlates with nanoribbon orientation, while non-textured films exhibit the strongest microstrain aggregation.

Outlook and future work

Building upon these findings, several directions can be pursued to advance Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ toward higher-efficiency devices and broader applications. Significantly higher efficiencies can be achieved through systematic interface engineering, absorber thickness optimization, and exploration of alternative ETLs (TiO_2 , ZnO , SnO_2) and device architectures such as n-i-p configurations, drawing on the composition-specific growth regimes and texture baselines established in this work. For Bi_2S_3 and Bi-rich compositions, which are n-type, p-type doping and careful selection of heterojunction partners with suitable band alignment remain largely unexplored and could enable p-n devices with improved carrier separation and performance. Beyond single-junction thin-film solar cells, the bandgap tunability across the solid-solution series offers potential for tandem photovoltaics and indoor energy harvesting, while the cross-verified texture characterization pipeline – combining BBXRD-derived analytical parameters with pole figures and EBSD validation – can be extended to other Q1D chalcogenide systems in photocatalysis and related optoelectronic applications.

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Abstract

Development of Bi_2S_3 -based materials by close-spaced sublimation for thin-film solar cell applications

Quasi-one-dimensional (Q1D) antimony and bismuth chalcogenides – Sb_2S_3 , Sb_2Se_3 , Bi_2S_3 , and their solid solutions, including $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ – are an emerging class of absorber materials for thin-film photovoltaic (PV) devices. They possess an orthorhombic crystal structure with $[\text{C}_4\text{A}_6]_n$ nanoribbons held together by van der Waals forces, with benign grain boundaries and strongly anisotropic carrier transport. The orientation of nanoribbons relative to the substrate is one of the key parameters for efficient charge transport in antimony and bismuth chalcogenide thin-film solar cells. PCEs of 8.36% for Sb_2S_3 , 10.58% for Sb_2Se_3 , and 11.02% for $\text{Sb}_2(\text{S}_y\text{Se}_{1-y})_3$ have been reported; however, the bismuth-based Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution system remained less studied, with close-spaced sublimation (CSS) deposition not yet applied to either material system.

The aim of this doctoral thesis is to study and develop the CSS deposition protocols for Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ (with different $[\text{Sb}]:[\text{Bi}]$ ratios) and provide an understanding of the impact of CSS deposition conditions on thin-film properties, including the morphological, structural, and optoelectronic parameters of the films, and demonstrate their applicability in proof-of-concept solar cells.

The thesis is based on three peer-reviewed publications and comprises three chapters. Chapter 1, "Literature review", provides a brief review of the history of photovoltaics, followed by the general overview of the Q1D chalcogenide PV materials with a focus on bismuth-based Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, depicting both the present pool of knowledge on these materials and identification of key knowledge gaps. Chapter 2 provides the details on both the sample manufacturing (solid solution synthesis, fabrication of thin films and solar cells) and the characterization techniques employed in this study. Chapter 3 is based on the results of Publications I-III and is divided into three sections that contain original experimental results and corresponding discussions. Section 3.1., based on Publication I, reports the first CSS deposition of Bi_2S_3 thin films, optimization of deposition conditions on glass and functional PV substrates (TiO_2 and CdS), and the characterization of resulting films and solar cell devices, including a defect study by low-temperature photoluminescence (PL). Section 3.2., based on Publication II addresses the synthesis of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions with five $[\text{Sb}]:[\text{Bi}]$ ratios, their CSS deposition as thin films, composition-dependent optoelectronic characterization, the first PL study of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions, and a proof-of-concept solar cell device. Section 3.3, based on Publication III, investigates the texture and structural properties of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films using a comprehensive set of X-ray diffraction techniques and electron backscatter diffraction (EBSD).

CSS deposition conditions for Bi_2S_3 thin films on glass were optimized by varying the source temperature ($T_{\text{so}} = 450\text{--}600\text{ }^\circ\text{C}$), the substrate temperature ($T_{\text{sub}} = 200\text{--}450\text{ }^\circ\text{C}$), and the deposition time. At $T_{\text{so}} = 550\text{ }^\circ\text{C}$ and $T_{\text{sub}} = 400\text{--}450\text{ }^\circ\text{C}$, uniform Bi_2S_3 thin films with preferential $h1l$ ($Pnma$) orientation were obtained. Under all conditions, Bi_2S_3 films maintain n-type conductivity with electron concentrations of $10^{16}\text{--}10^{17}\text{ cm}^{-3}$ and mobilities of $4.0\text{--}8.0\text{ cm}^2/\text{V}\cdot\text{s}$. For a proof-of-concept PV device, dense Bi_2S_3 films were fabricated onto CdS and TiO_2 electron transport layers (ETLs) with the stacks of glass/FTO/ CdS and glass/FTO/ TiO_2 at higher deposition rates than on bare glass. Superstrate configuration devices with glass/FTO/ $\text{CdS}/\text{Bi}_2\text{S}_3/\text{Au}$ and

glass/FTO/TiO₂/Bi₂S₃/Au architectures yielded PCEs of ~0.1% and ~0.3%, respectively, limited by the n–n isotype heterojunction and unsuitable/defective ETL-absorber interface. Low-temperature PL analysis revealed three emission bands in CSS-deposited Bi₂S₃: B₁ at 1.13 eV, B₂ at 0.86 eV, and B₃ at 1.23 eV. Based on the temperature-dependent band shifts and activation energies extracted from Arrhenius plots, a Deep Donor to Deep Acceptor (DD–DA) recombination model was proposed. It is shown that Bi₂S₃-based n–n isotype heterojunction devices are mainly limited by the reduced carrier collection at the weak built-in electric field.

(Sb_xBi_{1-x})₂S₃ solid solutions with $x = 0.1, 0.33, 0.5, 0.67, \text{ and } 0.9$ were synthesized from binary Sb₂S₃ and Bi₂S₃ powders and deposited as thin films by CSS. Through solid-solution ingot synthesis combined with thermodynamically guided CSS screening, composition-dependent growth regimes were identified that enable the reproducible formation of dense, homogeneous absorber layers across the entire (Sb_xBi_{1-x})₂S₃ solid solution compositional range. The chemical composition of the deposited films stayed within 3.5 at% of the targeted [Sb]:[Bi]:[S] ratios. Hall-effect measurements revealed a composition-dependent transition from n-type conductivity in Bi-rich films (resistivity ~5 Ω·cm, carrier concentration ~10¹⁷ cm⁻³) to p-type conductivity in Sb-rich films (resistivity up to ~10⁶ Ω·cm). Energy-resolved electrochemical impedance spectroscopy (ER-EIS) demonstrated that already a small Bi incorporation, corresponding to (Sb_{0.9}Bi_{0.1})₂S₃, transforms the deep mid-gap defect states characteristic of Sb₂S₃ into shallow ones while preserving Sb₂S₃-like band-edge positions – a defect "healing" effect through cation substitution. Both direct and indirect optical transitions were observed, with direct bandgaps varying semi-linearly from 1.3 eV (Bi₂S₃) to 1.7 eV ((Sb_{0.9}Bi_{0.1})₂S₃) and indirect bandgaps from 0.9 to 1.25 eV – the first experimental confirmation of theoretically predicted indirect transitions in this system. Low-temperature PL spectra of (Sb_xBi_{1-x})₂S₃ solid solutions, reported here for the first time, exhibit broad asymmetric emission bands consistent with radiative recombination through shallow localized states rather than deep defect levels, in agreement with the ER-EIS findings. CSS deposition conditions were individually optimized for each composition – including a refinement of the Bi₂S₃ protocol to lower T_{so} and slower deposition rates. A proof-of-concept glass/FTO/CdS/(Sb_{0.9}Bi_{0.1})₂S₃/Au device yielded $V_{OC} = 581$ mV, $J_{SC} = 6.62$ mA/cm², FF = 35.6%, and PCE = 1.37%, which is a considerable improvement over the binary Bi₂S₃ devices, with a nearly three-fold increase in V_{OC} . The device retained ~85% of its initial PCE after six months of unencapsulated storage in air.

Comprehensive texture analysis was performed using advanced Bragg–Brentano XRD (BBXRD) analytical parameters – texture coefficient (TC) and ribbon carrier transport (RCT) – grazing-incidence XRD (GIXRD) for depth-resolved structural information, texture XRD (pole figures) for full orientation distributions, and EBSD mapping for grain-level orientation analysis. This set of techniques provided a reproducible assessment of nanoribbon orientation, revealing trends in preferred orientation as a function of both [Sb]:[Bi] ratio and CSS deposition conditions across the full composition range. In the films with the most vertical nanoribbon orientation, nanoribbons were oriented at $\alpha' = 34.6^\circ\text{--}52.5^\circ$ relative to the substrate normal, with the best verticality (34.6°) found in (Sb_{0.5}Bi_{0.5})₂S₃. The composition-dependent texture evolution is proposed to originate from the interplay between CSS deposition kinetics and the progressive increase in lone-pair stereoactivity upon Sb substitution, which enhances the bonding anisotropy and promotes preferential nanoribbon alignment. GIXRD depth profiling of six compositions

showed that lattice parameters and microstrain vary through film thickness, with their depth-dependent evolution correlating with nanoribbon orientation.

Based on these findings, the thesis provides a promising methodology for the development of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films by CSS, showing step-by-step strategies for the optimization and refinement processes to achieve homogeneous absorber layers with dense morphology and optimal nanoribbon orientation for solar cell applications. A complementary set of advanced characterization tools was applied to understand the structural, optoelectronic, and defect properties of the deposited films and their correlation with CSS deposition conditions. The key novelty of the thesis comprises: (i) thermodynamically-guided CSS processing for the development of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin film absorbers; (ii) defect analysis in CSS-deposited Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions by low-temperature photoluminescence, providing the first insights into possible recombination pathways; (iii) development of a multi-technique texture characterization methodology combining BBXRD, texture XRD, and EBSD for Q1D chalcogenide thin films, allowing in-depth texture analysis and showing that nanoribbon orientation across the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ composition range can be controlled by the tuning of CSS deposition conditions; (iv) demonstration of the first proof-of-concept devices with $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ absorber by CSS.

Kokkuvõte

Bi₂S₃-põhiste materjalide väljatöötamine lähidistants-sublimateerimise meetodil kasutamiseks õhukesekilelistes päikesepatareides

Kvaasi-ühemõõtmelised (Q1D) antimoni ja vismuti kalkogeniidid – Sb₂S₃, Sb₂Se₃, Bi₂S₃ ning nende tahked lahused, sealhulgas (Sb_xBi_{1-x})₂S₃ – on uudne absorbermaterjalide klass õhukesekileliste päikesepatareide (ingl *photovoltaics*, PV) jaoks. Nendel materjalidel on ortorombiline kristallstruktuur, mis koosneb van der Waalsi jõududega seotud [C₄A₆]_n nanoribadest, mistõttu on materjalil anisotroopsed omadused. Nanoribade orientatsioon substraadi suhtes on üks keskseid tegureid, mis määrab laengkandjate tõhusa transpordi antimoni- ja vismutipõhistes kalkogeniidsetes õhukesekilelistes päikesepatareides. Kui Sb₂S₃, Sb₂Se₃ ja Sb₂(S_ySe_{1-y})₃ -põhiste seadiste kasutegurid on vastavalt 8,36%, 10,58% ja 11,02% siis Bi₂S₃ ning (Sb_xBi_{1-x})₂S₃ tahkete lahuste põhiseid seadiseid on märksa vähem uuritud. Lisaks sellele puuduvad uuringud Bi₂S₃ ning (Sb_xBi_{1-x})₂S₃ absorberkihtide valmistamise kohta lähidistants-sublimateerimise (ingl *close-spaced sublimation*, CSS) meetodil.

Doktoritöö eesmärk on uurida ja arendada Bi₂S₃ ning erinevate [Sb]:[Bi] suhetega (Sb_xBi_{1-x})₂S₃ ühendite õhukeste kilede sadestamist CSS-meetodil ning anda terviklik ülevaade sellest, kuidas sadestustingimused mõjutavad kilede morfoloogilisi, struktuurseid ja optoelektronilisi omadusi ning milline on nende materjalide rakendatavus päikesepatareides.

Töö tugineb kolmele eelretsenseeritud teaduspublikatsioonile ning koosneb kolmest peatükist. Esimene peatükk annab lühikese ülevaate päikesepatareide arenguloost ja käsitleb üldisemalt Q1D kalkogeniidseid PV-materjale, keskendudes seejuures vismutipõhistele Bi₂S₃ ja (Sb_xBi_{1-x})₂S₃ ühenditele, tuues esile senise teadmistepagasi ja peamised teadmislüngad. Teine peatükk kirjeldab proovide valmistamist, sealhulgas tahkete lahuste sünteesi, õhukeste kilede ja päikesepatareide valmistamist, ning kasutatud karakteriseerimismeetodeid. Kolmas peatükk põhineb publikatsioonide I–III tulemustel ning jaguneb kolmeks alapeatükiks, mis sisaldavad originaalseid katsetulemusi ja nende arutelu. Alapeatükk 3.1, mis põhineb publikatsioonil I, käsitleb Bi₂S₃ õhukeste kilede sadestamist CSS-meetodil, sadestustingimuste optimeerimist erinevatel substraatidel ning saadud kilede ja päikesepatareide karakteriseerimist, sealhulgas defektide uurimist madalatemperatuurilise fotoluminestsentsi abil. Alapeatükk 3.2 põhineb publikatsioonil II ja käsitleb viie erineva [Sb]:[Bi] suhtega (Sb_xBi_{1-x})₂S₃ pulbriliste tahkete lahuste sünteesi, ja nendest õhukeste kilede sadestamist CSS-meetodil, koostisest sõltuvat optoelektroniliste omaduste karakteriseerimist, (Sb_xBi_{1-x})₂S₃ tahkete lahuste esmakordset fotoluminestsentsuuringut ning päikesepatarei valmistamist. Alapeatükk 3.3, põhineb publikatsioonil III ja käsitleb (Sb_xBi_{1-x})₂S₃ õhukeste kilede struktuurseid ja tekstuuri omadusi, kasutades selleks erinevaid röntgendifraktsioonil põhinevaid meetodeid ning elektronitagasihajumise difraktsiooni (ingl *electron backscatter diffraction*, EBSD).

Bi₂S₃ õhukeste kilede sadestustingimusi klaassubstraatidele optimeeriti läbi lähteaine temperatuuri (T_{so} = 450–600 °C), substraadi temperatuuri (T_{sub} = 200–450 °C) ja

sadestusaja muutmise. Ühtlased Bi_2S_3 kiled kristallitide eelistatud $h1l$ ($Pnma$) orientatsiooniga saadi kui kilede valmistamiseks kasutati $T_{so} = 550\text{ }^\circ\text{C}$ ja $T_{sub} = 400\text{--}450\text{ }^\circ\text{C}$. Kõikidel uuritud tingimustel säilis Bi_2S_3 kilede n-tüüpi juhtivus, elektronide kontsentratsioon oli $10^{16}\text{--}10^{17}\text{ cm}^{-3}$ ning liikuvus $4,0\text{--}8,0\text{ cm}^2/\text{V}\cdot\text{s}$. PV-seadiste valmistamiseks sadestati tihedad Bi_2S_3 kiled CdS ja TiO_2 elektrontranspordikihtidele (ingl *electron transport layer, ETL*), kasutades kihilisi alusstruktuure klaas/FTO/CdS ja klaas/FTO/ TiO_2 . Superstraat-tüüpi seadised klaas/FTO/CdS/ Bi_2S_3 /Au ja klaas/FTO/ TiO_2 / Bi_2S_3 /Au saavutasid kasuteguri vastavalt 0,1% ja 0,3%. Seadise jõudlust piirasid n–n isotüüpne heterosiire ning sobimatu või defektne ETL/ Bi_2S_3 piirpind. Madalatemperatuuriline fotoluminestsentsanalüüs näitas CSS-meetodil sadestatud Bi_2S_3 kiledes kolme emissioonimaksimumi: B_1 väärtusel 1,13 eV, B_2 väärtusel 0,86 eV ja B_3 väärtusel 1,23 eV. Temperatuurist sõltuvate piikide nihete ja Arrheniuse graafikutest saadud aktivatsioonienergiate põhjal pakuti välja sügava doonori ja sügava aktseptori vahelise rekombinatsiooni mudel. Näidati, et Bi_2S_3 -põhiste n–n isotüüpsete heterosiiretega seadiste peamine piirang tuleneb nõrga sisemise elektrivälja tõttu vähenenud laengukandja kogumisest.

$(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ pulbrilised tahked lahused koostistega $x = 0,1; 0,33; 0,5; 0,67$ ja $0,9$ sünteesiti binaarsetest Sb_2S_3 ja Bi_2S_3 pulbritest ning kasutati õhukeste kilede sadestamiseks CSS-meetodil. Kombineerides tahke lahuse kristallide valandi sünteesi ja CSS protsessi termodünaamilisi arvutusi määrati koostisest sõltuvad kasvurežiimid, mis võimaldasid reprodutseeritavalt moodustada tihedaid ja homogeenseid $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ absorberkihte. Halli mõõtmised näitasid koostisest sõltuvat üleminekut n-tüüpi juhtivuselt vismutirikastes kiledes (eritakistus $\sim 5\text{ }\Omega\cdot\text{cm}$, laengukandjate kontsentratsioon $\sim 10^{17}\text{ cm}^{-3}$) p-tüüpi juhtivusele antimonirikastes kiledes (eritakistus kuni $\sim 10^6\text{ }\Omega\cdot\text{cm}$). Energiataseme järgi lahutatud elektrokeemiline impedantspektroskoopia (ingl *energy-resolved electrochemical impedance, ER-EIS*) näitas, et juba väike Bi lisandumine koostisesse $(\text{Sb}_{0,9}\text{Bi}_{0,1})_2\text{S}_3$ muudab Sb_2S_3 -le iseloomulikud sügavad defektid keelutsoonis madalateks, säilitades samas Sb_2S_3 -le iseloomulikud tsooniservade positsioonid, mis viitab defektide energeetilisele ümberkorraldusele katioonasenduse kaudu. Täheldati nii otseseid kui ka kaudseid optilisi üleminekuid: otsese ülemineku keelutsooni laius muutus poollineaarselt väärtuselt 1,3 eV (Bi_2S_3) kuni 1,7 eV-ni ($(\text{Sb}_{0,9}\text{Bi}_{0,1})_2\text{S}_3$), kaudsete ülemineku keelutsoon aga vahemikus 0,9–1,3 eV. Käesolevale süsteemile on saadud tulemus esimene eksperimentaalne kinnitus teoreetiliselt varasemalt ennustatud kaudsetele üleminekutele. Esmakordselt esitatud $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ tahkete lahuste madalatemperatuurilised fotoluminestsentsspektrid näitasid laiu asümmeetrilisi emissioonimaksimume, mis on kooskõlas radiatiivse rekombinatsiooniga madalate lokaliseeritud seisundite kaudu, mitte sügavate defektide kaudu, mis on kooskõlas ER-EIS tulemustega. Kile iga koostise jaoks optimeeriti CSS-sadestustingimused eraldi, sealhulgas täiendati Bi_2S_3 sadestusprotokolli madalama T_{so} ja aeglasema sadestuskiirusega. PV-seadise klaas/FTO/CdS/ $(\text{Sb}_{0,9}\text{Bi}_{0,1})_2\text{S}_3$ /Au väljundparameetrid nagu $V_{oc} = 581\text{ mV}$, $J_{sc} = 6,62\text{ mA}/\text{cm}^2$, $FF = 35,6\%$ ja $PCE = 1,37\%$ näitavad märkimisväärset paranemist võrreldes Bi_2S_3 seadisega, sealhulgas ligi kolmekordset avatud ahela pinget (ingl *open circuit voltage, V_{oc}*) kasvu. Seadis säilitas ligikaudu 85% oma algsest kasutegurist pärast kuue kuu pikkust kapseldamata hoiustamist õhus.

Õhukeste kilede kristallstruktuuri analüüsiks kasutati mitmete meetodite kombinatsiooni sealhulgas Bragg–Brentano röntgendifraktsiooni (BBXRD) koos tekstuurikoefitsiendi (TC) ja nanoribade laengukandja transpordi (ingl ribbon carrier transport, RCT) analüüsiga, libiseva kiire röntgendifraktsiooni (ingl grazing incidence X-ray diffraction, GIXRD), XRD tekstuurimõõtmisi koos poolusjoonistega ning tagasihajunud elektronide difraktsiooni (EBSD). Tulemused näitasid, et $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ õhukestes kiledes sõltub kristalliitide eelorientatsiooni [Sb]:[Bi] suhtest ja CSS-sadestustingimustest. Vertikaalseim nanoribade orientatsioon substraadi suhtes ($34,6^\circ$) saavutati $(\text{Sb}_{0,5}\text{Bi}_{0,5})_2\text{S}_3$ koostisega õhukeses kiles.

Kokkuvõttes annab käesolev doktoritöö tervikliku metoodilise aluse Bi_2S_3 ja $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ õhukeste kilede arendamiseks CSS-meetodil, näidates samm-sammult optimeerimis- ja täiustamisstrateegiaid homogeensete, tiheda morfoloogiaga ja päikesepatareirakenduste jaoks sobiva nanoribade orientatsiooniga absorberkihtide saamiseks. Täiendavalt kasutati laia valikut karakteriseerimismeetodeid, et mõista sadestatud kilede struktuurseid, optoelektronilisi ja defektidega seotud omadusi ning nende seoseid CSS-sadestustingimustega. Töö peamised uudsusaspektid on: (i) termodünaamiliselt juhitud CSS-protsesside väljatöötamine Bi_2S_3 ja $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ õhukeselekileliste absorberite jaoks; (ii) CSS-meetodil sadestatud Bi_2S_3 ja $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ õhukeste kilede defektianalüüs madalatemperatuurilise fotoluminestsentsi abil, mis annab esmased teadmised võimalike rekombinatsioonimehhanismide kohta; (iii) Q1D kalkogeniidsete õhukeste kilede tekstuurianalüüs mitme meetodi kombinatsioonina, ühendades BBXRD, XRD ja EBSD analüüsimeetodid; (iv) ning esimeste CSS-meetodil valmistatud $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ -absorberiga päikesepatareide demonstreerimine.

Appendix 1

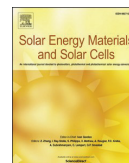
Publication I

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journal homepage: www.elsevier.com/locate/solmatDevelopment of Bi₂S₃ thin film solar cells by close-spaced sublimation and analysis of absorber bulk defects via in-depth photoluminescence analysisM. Koltsov^a, S.V. Gopi^a, T. Raadik^a, J. Krustok^a, R. Josepson^b, R. Gržibovskis^c, A. Vembris^c, N. Spalatu^{a,*}^a Department of Materials and Environmental Technology, Tallinn University of Technology, Ehitajate tee 5, Tallinn, Estonia^b Division of Physics, Tallinn University of Technology, Ehitajate Tee 5, 19086, Tallinn, Estonia^c Institute of Solid State Physics, University of Latvia, Kengaraga Str. 8, Riga, Latvia

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ABSTRACT

The emergence of new PV applications in society requires the design of new materials and devices based on green and earth-abundant elements, with a different set of properties and wider applicability. In this perspective, Bi₂S₃ semiconductor material have gained attention as a defect-tolerant, non-toxic, and highly stable material for earth-abundant thin film PV technologies. Related to Bi₂S₃ non-toxic nature, so far it has been very popular to synthesize the material by chemical solution routes, while little research efforts have been dedicated to absorber deposition by physical deposition techniques. In particular, there are no studies on absorber development via rapid, high-volume, and in-line close-spaced sublimation technique. Moreover, in-depth analysis of material defects employing low temperature-dependent photoluminescence (PL) remains largely unexplored. In this work, we systematically study the impact of close-spaced sublimation (CSS) conditions on Bi₂S₃ absorber growth on various substrates, employing a wide range of source (400–600 °C) and substrate (200–400 °C) temperatures. CSS source temperature of 550 °C and substrate temperature of 400–450 °C were identified as optimal temperatures (grown either on glass, TiO₂, or CdS substrates), allowing the fabrication of uniform and dense Bi₂S₃ films with enhanced [221]-oriented grains. For the first time, a proof of concept solar cell with CSS Bi₂S₃ is demonstrated and an in-depth analysis on the interrelation between grain structure, interface recombination, and device performance is provided. Employing low-temperature dependence PL, new and complementary insights on possible defects and recombination mechanisms are presented.

1. Introduction

Bismuth chalcogenides (Bi-CAL) such as Bi₂S₃, Sb₂BiSe₃, CuBiS₂, AgBiS₂, and other related derivatives are identified as a new class of emerging photovoltaic (PV) materials [1,2]. Bi₂S₃ material has a number of distinct advantages such as a high absorption coefficient (10⁵ cm⁻¹, and absorption onset in the infrared) [1], exhibits both n-type [3] and p-type conductivity [4], bandgap lies in the optimal region for PV and can be varied from 1.1 eV to 1.7 eV, due to quantum confinement effects and/or stoichiometry variations [1–4]. In addition, bismuth is an abundant metal on the Earth's crust; it is a by-product of Pb, Cu, and Sn refining and has significant commercial applications, resulting in the price of Bi being relatively low and stable [5,6]. Along with other emerging PV materials [2,7], bismuth is considered non-toxic and is even used in common medicines such as Pepto-Bismol [8]. Furthermore,

Bi₂S₃ has been suggested as an excellent candidate for defect-tolerant compounds (i.e., materials with good optoelectronic properties despite the presence of defects); it crystallizes in the orthorhombic system where a 1D anisotropic lattice structure comprised of “nano-ribbons”, held together via Van-der-Waals forces. This means no breaking of the lattice is required for termination at grain boundaries in Bi-CAL, making them grain boundary defect tolerant [1,2,9].

Defect tolerance is a key property of promising PV materials, especially for indoor PV applications where the defects in the PV can render a solar cell inoperable at indoor light levels. Despite of Bi-CAL PV material having this great advantage, its potential for indoor PV applications remains largely unexplored. Related to Bi₂S₃'s non-toxic nature, so far it has been very popular to deposit the material by chemical solution routes such as chemical bath deposition [10], chemical vapor deposition (CVD) [11], metal-organic CVD (MOCVD) [12] as well and successive

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ionic layer adsorption and reaction (SILAR) [13]. Several reports demonstrated the potential of Bi-CAL materials in solar cells, using most often chemical methods, including colloidal Bi_2S_3 nanocrystals (NCs) [14,15], Bi_2S_3 active layer inorganic/inorganic bulk heterojunction solar cells (Bi_2S_3 nanowires) [16], Cu_3BiS_3 as a thin film [17] and sensitizer in dye-sensitized TiO_2 solar cells [18], and CuBiS_2 as nanoparticles [19]. Solar cell devices with a PCE of 5% have been realized by blending Bi_2S_3 NCs and PbS QDs to form a bulk nano-heterojunction structure which is the state of the art for such device architecture [15]. To date, the highest PCE for Bi-chalcogenide-based solar cell has approached 7% employing $\text{Cu}_4\text{Bi}_4\text{S}_9$ alloy as an absorber [20]. Significant research efforts were dedicated to the modification in the solar cell structure, however, this is not the only possible strategy to improve PCE. One significant drawback in all mentioned above Bi_2S_3 NCs-based heterojunction structures is that nanocrystals are randomly oriented in the films. Therefore, some of the NCs will be properly placed for conducting charges, while others will not, limiting charge transport and device PCE [1,12–15]. One strategy to overcome this limit is to take advantage of the naturally anisotropic, low-dimensional crystalline structures of Bi_2S_3 and to develop thin films with aligned 1D structures like nanoribbons. Such an approach will optimize the carrier transport through the growth of properly aligned and connected 1D ribbon structures and hence improve the thin film solar cell PCE. Although the such approach is widely used in other emerging chalcogenide PV materials with a similar 1D anisotropic ribbon structure like SnS , Sb_2Se_3 , Sb_2S_3 , and their alloys $\text{Sb}_2(\text{S},\text{Se})_3$ [21–24], it has been scarcely explored for Bi_2S_3 , particularly for thin film device configuration.

Few strategies to create aligned Bi_2S_3 1D nanoribbon structures have been developed with bulk-heterojunction architectures achieving a promising 3.3% PCE [16]. The PCE of Bi-CAL-based solar cells is still low despite of predicted 30% theoretical PCE limit [1]. To make further progress in the PCE of Bi-CAL solar cells, absorber qualities such as composition morphology, crystallinity, crystallite orientation, bandgap, mobility, conductivity, carrier densities, doping density, and film density must be optimized. Also, the interfaces must be optimized to reduce the number of defects and recombination in a solar cell. Moreover, research investigations on the development of the Bi-CAL thin film as well as the solar cell structures by physical deposition methods are quite rare among the literature. Bi_2S_3 film was, supposedly, first deposited by physical methods in 1998 by Rincón et al. [10], heating the source material up to 900 °C and applying temperatures between 25 °C and 300 °C to the substrate. In the context of thin-film photovoltaic applications, Haaf et al. [25] employed physical deposition of Bi_2S_3 for the first time, ranging the temperature of substrate from 80 °C to 290 °C. Therein by using confocal photoluminescence, the authors showed the advantages of high-temperature deposition in terms of optical properties. Song et al. [26] used rapid thermal evaporation to produce a Bi_2S_3 absorber layer for ITO/p-NiO/n- Bi_2S_3 /Au solar cells, with source temperature around 600 °C and substrate temperatures between 100 °C and 300 °C, demonstrating a power conversion efficiency of 0.75%.

To the best of our knowledge, there are little to no reports in the literature regarding the deposition of Bi_2S_3 thin films and solar cells via close-spaced sublimation (CSS), which appeared to be a reasonable research gap to fill. In addition, there is a limited number of studies dedicated to defect analysis in the bulk of Bi_2S_3 thin films, employing advanced low-temperature dependence photoluminescence (PL) technique. In this context, the aim of the current study is to systematically investigate the impact of CSS processing conditions on the properties of Bi_2S_3 thin film absorber deposited on various substrates and to analyze the interrelation between the changes in the absorber properties and device performance. The novelty lies in the applied systematical technological approach, employing a large variation of the processing source and substrate temperatures, towards the identification of optimal CSS deposition conditions to produce uniform films with suitable orientation on various substrate partner layers. Comprehensive analysis of the structural and morphological changes in the absorber deposited on

various substrates and correlation with the device efficiency is provided. Moreover, for the first time, we bring in-depth insights on defects and possible recombination mechanism in Bi_2S_3 absorber films employing low-temperature dependence photoluminescence measurements.

2. Experimental

2.1. Bi_2S_3 thin-film fabrication

Bi_2S_3 thin films were deposited atop of four different types of substrate: roughen microscopic glass (O.Kindler one end double frost microscopic glass, 1 mm thickness), plain glass (backside of Sigma-Aldrich FTO glass used, 2 mm thickness), glass/FTO/ TiO_2 , and glass/FTO/CdS stacks. CdS buffer layers were deposited onto Sigma-Aldrich FTO glass by a conventional chemical bath deposition (CBD) technique [27]. TiO_2 buffer layers were deposited on the same FTO glass by ultrasonic spray pyrolysis (USP) [28]. Bi_2S_3 films were deposited with a custom-made close-spaced sublimation (CSS) reactor from a Bi_2S_3 powder (Alfa Aesar, 5 N) under a vacuum of 10^{-4} Pa. To develop optimal CSS processing conditions which would allow fabricating of dense and compact absorber film, a systematical technological approach was adopted in which the CSS source temperature was varied between 450 °C and 600 °C, while for each source temperature, the substrate temperature was varied from 200 °C to 450 °C. The CSS temperature profile and ramping are schematically presented in Fig. 1.

2.2. Material and device characterization

X-ray diffraction (XRD) patterns were taken using a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.54$ Å, 40 kV, 40 mA). A Zeiss HR-SEM MERLIN scanning electron microscope (SEM) with the GEMINI II column was used for the top- and cross-sectional view of the structures. Raman measurements were performed with a Horiba Jobin Yvon Labram HR 800 spectrometer ($\lambda = 532$ nm). The resistivity, charge carrier concentration, and mobility of the Bi_2S_3 films were measured at room temperature using MMR's variable-temperature Hall system and a Hall and van der Pauw controller H-50. The in-plane resistivity and electron densities were calculated for thicknesses of 0.5–1 μm , which were estimated from the SEM analysis. Each measurement was carried out 5 times and the mean value was taken. J-V curves were measured for Bi_2S_3 devices with a Wavelabs LS-2 LED solar simulator (100 mW cm^{-2} , AM1.5) at room temperature in ambient air. External quantum efficiency (EQE) spectra were measured with a monochromatized light source (Newport 300 W Xenon lamp, Newport Cornerstone 260 monochromator), a Merlin digital lock-in detector, and a factory-calibrated Si reference detector. The ionization potential and electron affinities of the thin films in the device stack were determined by the photoelectron emission spectroscopy technique, to ascertain the band alignment. A 0.64 m focal length single grating (600 mm^{-1}) monochromator and the 442 nm line of a He-Cd laser with different powers were used for PL measurements. For PL signal detection, a Hamamatsu InGaAs photomultiplier tube (PMT) was used. A closed-cycle helium cryostat was employed to measure temperature dependencies of the PL spectra at temperatures from 20 to 300 K. The laser spot size for these measurements was 200 μm in diameter.

3. Results and discussion

3.1. Structural properties of Bi_2S_3 films

Bi_2S_3 films deposited by CSS onto four different substrates – roughen microscopic glass, plain glass on the backside of FTO substrate, glass/FTO/ TiO_2 (further just TiO_2), and glass/FTO/CdS (further just CdS) stacks. A large series of Bi_2S_3 absorber layers were initially deposited on roughen glass substrate with the aim to identify the most optimal CSS source (T_{so}) and substrate temperatures (T_{sub}) which would allow a

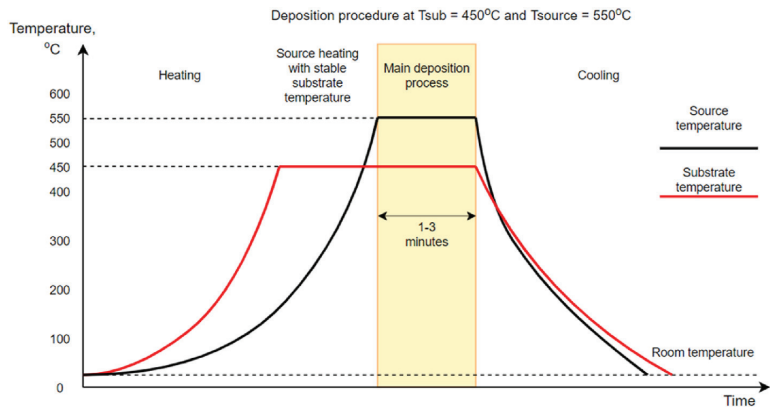


Fig. 1. Schematic representation of the CSS deposition temperature profile and ramping.

reasonable deposition rate and lead to the formation of compact and dense films. The roughened glass plates with a root-mean-square roughness, R_q , of 2.66 nm (Sigma-Aldrich) were used to ensure better adhesion of the Bi_2S_3 absorber films and also to perform electrical measurements. After the identification of the optimal source temperature, the absorber was deposited onto different substrates (including plain glass, $\text{TiO}_2/\text{FTO}/\text{glass}$, and $\text{CdS}/\text{FTO}/\text{glass}$ substrates) with the variation of the substrate temperature between 200 and 450 °C in steps of $\Delta T = 50$ °C. Information about deposition conditions for different substrates is summarized in Table 1. All Bi_2S_3 films deposited on various substrates were first characterized by XRD and Raman spectroscopy. Fig. 1 (a,c,e) shows XRD patterns of Bi_2S_3 films deposited onto rough glass, which were indexed and assigned to orthorhombic Bi_2S_3 crystal structure with $Pbnm$ space group symmetry (JCPDS 00-017-0320) [29].

For a better qualitative analysis of the preferential orientation of the crystallite along specific crystalline planes, the texture coefficient (TC) was calculated (Fig. 2b,d,f) according to Eq. (1):

$$TC(hkl) = \frac{I(hkl)}{I_0(hkl)} \times \left[\frac{1}{N} \sum_{i=0}^N \frac{I(hkl)}{I_0(hkl)} \right]^{-1} \quad (1)$$

where $I(hkl)$ is the measured intensity for a given reflection with hkl indices, $I_0(hkl)$ is a reference intensity for a given reflection acquired from the JCPDS Card No. 00-017-0320, and N is the number of reflections considered in the analysis [30].

It can be seen that for a given T_{so} , the values of TC change differently depending on T_{sub} . At $T_{so} 500$ °C, (020) and (130) crystalline planes were dominant. When the T_{sub} was increasing, the values of TC increased for (020) and (130) planes, and at the same time along other major planes like (220) and (211), the TC values decreased. In the case of $T_{so} 550$ °C, the most prominent planes were (130), (310), and (211). Generally, it was difficult to distinguish some clear trend for the TC of (020), (220), and (130) planes, while the TC for (310), (211), and (221) planes had slightly grown along with the increase of T_{sub} . At $T_{so} 600$ °C, the most prominent planes were (310), (211), and (221) for which the TC values increased systematically when the T_{sub} increased from 200 to 350 °C. For the same T_{so} , at substrate temperatures higher than 350 °C the TC values of the same planes decreased.

Table 1
Deposition conditions for various substrates.

Substrate	Roughen glass	Plain glass	TiO_2	CdS
T_{so} , °C	450, 500, 550, 600	550	550	550
T_{sub} , °C	100–550	200–450	200–450	200–450
Deposition time, min	1	1, 2, 3, 5	1	1

For the next set of samples in which the Bi_2S_3 films were deposited on glass, CdS, and TiO_2 , the $T_{so} 550$ °C was chosen as the optimal source temperature, allowing an optimal deposition rate of $\sim 0.8\text{--}1$ $\mu\text{m}/\text{min}$. The choice for this temperature was also made based on a systematic source temperature screening for different substrates and according to XRD data the 550 °C source temperature led to the most prominent orientation of the crystallite along $(hkl, l = 1)$. In addition, when compared to $T_{so} 600$ °C, the $T_{so} 550$ °C also allowed better controllability of CSS deposition process and absorber layer thickness.

When performing the TC analysis of Bi_2S_3 deposited onto plain glass substrates at $T_{so} 550$ °C, no clear trend was found, except the decreasing of TC for the (221) plane with the increasing of substrate temperature from 250 to 450 °C. At the same time, in comparison with the films deposited onto rough glass there is a difference in the TCs of the films grown onto plain glass. This effect can be explained by different surface energy of these two substrates. In the case of rough glass, the higher surface energy can provide different conditions for the nucleation sites and adatom diffusion on the surface. This will affect the formation of islands, their coalescence and grain coarsening during the film growth and thus the orientation of the final grains in the layers. For the absorber deposited on TiO_2 substrates, with an increase in the substrate temperature, the TC were slowly decreasing for the (020), (220), (130), and (310) planes while increasing for the (221) plane. In the case of Bi_2S_3 films deposited on CdS substrate, the TC was slowly decreasing for (130) and (211) planes and increasing for (310) and (221) planes, as the substrate temperature increased from 250 to 450 °C (see Fig. 3). It is important to mention that according to XRD results, at T_{so} below 500 °C the film seemed mostly amorphous with very few distinguishable peaks (Fig. S1, Supplementary material). On another hand, a very interesting observation is that in the XRD pattern of Bi_2S_3 deposited with $T_{so} \sim 600$ °C and $T_{sub} \sim 450\text{--}500$ °C, separated phases of Bi and Bi_2S_3 were detected (Fig. S2, Supplementary material), suggesting that at higher deposition temperature there was an excessive loss of sulfur from the system. Such a phenomenon can be explained by the higher partial pressure of sulfur at $T \geq 600$ °C which can easily generate sulfur poor conditions in the Bi_2S_3 system [31]. It should be noted that the phase composition of Bi_2S_3 was further analyzed by Raman measurements, as seen in Fig. S3, Supplementary material. For the $T_{so} 550$ °C, independent of the substrate temperature and the used substrate for the deposition of Bi_2S_3 films, Raman spectra showed similar vibrational modes, which correspond to the pure Bi_2S_3 phase [32].

Bi_2S_3 absorber films, deposited on all substrates, at low (250 °C) and high (450 °C) temperatures, were analyzed by scanning electron microscopy (SEM). Images of Bi_2S_3 films, deposited onto rough glass, are given in Fig. 4. It can be seen, that absorber layers deposited at higher

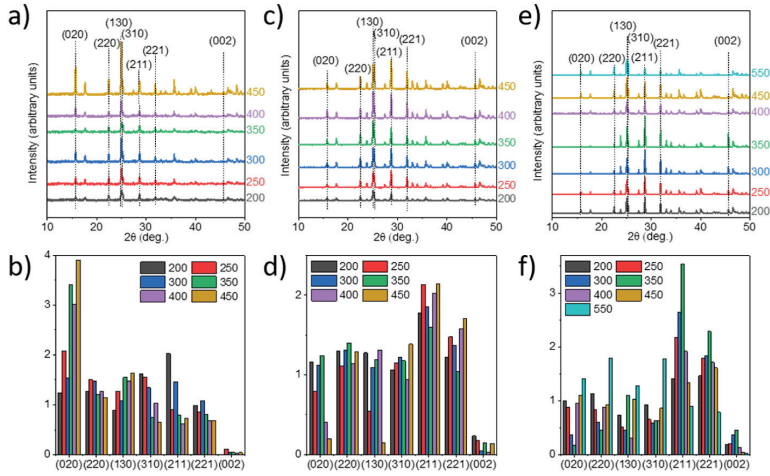


Fig. 2. XRD patterns of Bi_2S_3 absorber films deposited by CSS onto roughen glass substrates, at three source temperatures (T_{so}) – (a) 500 °C, (c) 550 °C, (e) 600 °C, and for each T_{so} , the substrate temperature varied between 200 °C and 550 °C in steps of $\Delta T = 50$ °C; (b, d, e) The corresponding TC values calculated from integrated intensity ratios for main crystal planes in Bi_2S_3 films.

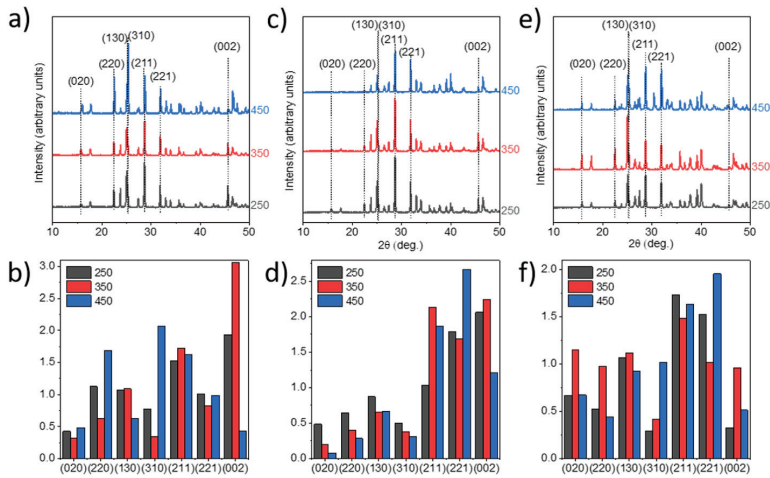


Fig. 3. XRD patterns of Bi_2S_3 absorber films deposited by CSS at $T_{\text{so}} 550$ °C and $T_{\text{sub}} 250$ °C, 350 °C and 450 °C onto various substrates – (a) plain glass, (c) TiO_2 and (e) CdS; (b, d, e) TC values calculated from integrated intensity ratios for main crystal planes in Bi_2S_3 films on respective substrates.

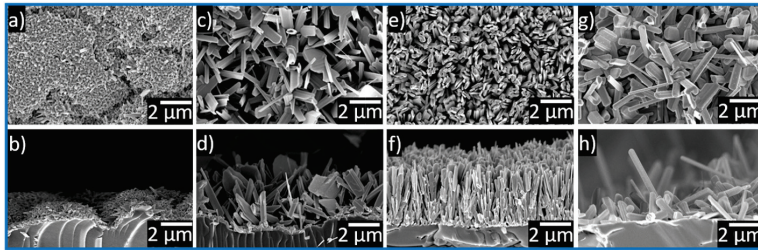


Fig. 4. (a, c, e, g) Top-view and (b, d, f, h) cross-sectional SEM images of Bi_2S_3 films deposited onto a roughen glass substrate at substrate temperature (T_{sub}) of (a, b) 200 °C, (c, d) 250 °C for 1 min deposition time, (e, f) T_{sub} of 250 °C for 3 min deposition time, and (g, h) T_{sub} of 450 °C for 1 min deposition time.

temperatures consists of larger grains compared to the films obtained at low-temperatures.

At 200 °C, the surface of the substrate was covered with a ~200 nm thick “seed” layer of small randomly-oriented grains (Fig. 4a and b). At higher temperatures (200–350 °C), needles and prism-like grains with no dominating orientation of growth were observed out of a minor portion of the seed layer (Fig. 4c and d). If deposition time in this temperature region was prolonged, more and more grains from the seed layer were able to grow into a needle (Fig. 4e and f). These needles were growing higher and more aligned as the thickness of the film increases from 3–4 μm to 4–5 μm, resulted from a change in the deposition time from 1 min (Fig. 4d) to 3 min (Fig. 4f). At high temperatures (400–450 °C), grains tend to coalesce, forming big randomly oriented “rods”, while the previously-existing seed layer is not visible anymore (Fig. 4g and h).

In the case of Bi₂S₃ deposited on plain glass, fewer nucleation centers were available on the substrate surface. This implies that a higher minimal T_{so} was required for the appearance of a first Bi₂S₃ thin film, compared with roughen glass - approximately 420 °C for roughen and 470 °C for plain glass substrates. At T_{so} 250 °C, the Bi₂S₃ films grow in a similar way to a film on roughen glass (Fig. 5a and b). At T_{so} 450 °C, a densely-packed morphology was observed in which grains grow in both lateral and longitudinal directions (Fig. 5c and d). In the case of prolonged deposition time, ~200 nm and ~600 nm thick films were obtained for 3 min (Fig. 5e and f) and 5 min (Fig. 5g and h) deposition time, respectively.

For Bi₂S₃ films, deposited on plain glass, TiO₂, and CdS at T_{sub} 250 °C, a similar morphology in which the films consisted of randomly-oriented needles and wide distribution by size (0.5–6 μm) was observed. At T_{sub} 450 °C, thick films of large, rather columnar grains were observed (Fig. 6d,h), with a similar formation mechanism seen in Fig. 5h. As a result of 1 min deposition, ~1 μm thick Bi₂S₃ films were observed onto TiO₂ and CdS substrates, while five times thinner (200 nm) film was observed on plain glass after 3 times longer deposition. The thicker film on TiO₂ and CdS can be explained by a higher nucleation sites density on the surface of both TiO₂ and CdS. It should be mentioned, that EDX analysis was conducted, focusing on the compositional maps of the cross section to check the homogeneity of the elemental distribution. No metallic elements or micro-inclusions of secondary phases were detected in the Bi₂S₃ films deposited at T_{so} 550 °C (Figs. S4 and S5, Supplementary material).

Based on the results of structural and morphological changes of Bi₂S₃ absorber layers depending on the CSS deposition conditions and use of various substrates, the following main conclusions can be drawn:

- i. Within the given set of source and substrate temperature regimes (T_{so}: 450 °C, 500 °C, 550 °C, and 600 °C; T_{sub}: 250 °C, 450 °C), the source temperature of 550 °C and substrate temperature 400–450 °C were identified as optimal temperatures which allowed reasonable deposition rate (~0.5–0.8 μm/min) and fabrication of uniform Bi₂S₃ films with a suitable (*hkl*, *l* = 1)

orientation independent whether the deposition was performed on either plain glass, TiO₂ or CdS as substrate;

- ii. At T_{so} below the optimal one, independent of the applied substrate temperatures, the absorber grains were predominantly oriented along (*hkl*, *l* = 0), while a high amount of amorphous phase was observed in Bi₂S₃ film grown at T_{so} 450 °C;
- iii. 600 °C source temperature was identified as a critical temperature, generating conditions for sulfur loss in the Bi₂S₃ system with the formation of separated metallic bismuth and Bi₂S₃ phases.

It is widely established for similar emerging inorganic chalcogenides such as Sb₂S₃ and Sb₂Se₃ absorbers that such a preferential (*hkl*, *l* = 1) orientation, obtained at T_{so} 550 °C and T_{sub} 450 °C for Bi₂S₃ film would be optimal for efficient charge transport and collection in the solar cell [33–36]. At this point, it is worth mentioning that several attempts investigated the properties of Bi₂S₃ deposited via physical deposition methods. Employing a thermal evaporation technique at T_{sub} between 25 °C and 285 °C, Haaf et al. [25] found that Bi₂S₃ films grown at temperatures right above the crystallization temperature exhibit a significant overrepresentation of reflections with indices (*hkl* *l* = 0), with a preferred growth along the *c*-axis parallel to the surface of the substrate. Therein only structural and optical properties were analyzed without the application of the absorber layer in a solar cell device. Following the same technological approach, Rincón et al. [10] obtained crystalline Bi₂S₃ film at T_{sub} 250–300 °C, however, with strong contribution in XRD patterns from (104), (012), and (003) planes of metallic bismuth. Therein the appearance of the separated phase was explained due to the nonstoichiometric dissociation of the S/Bi precipitate. Using a rapid thermal evaporation technique with a fast deposition rate (0.5 μm/min) at T_{sub} 100–300 °C, Song et al. [26] obtained crystalline, (023) (111) (122) oriented, compact Bi₂S₃ films. So far, this is the only study in which the Bi₂S₃ film deposited by physical deposition method was incorporated in solar cells with a demonstration of proof-of-concept device efficiency of 0.75%.

In terms of CSS processing temperature, our results seem to correlate with the findings by Song et al. [26], with the difference that in our case the optimal growth condition identified at a slightly higher substrate temperature and a general trend for the TC favorable towards grain orientation along (*hkl*, *l* = 1) planes. Having noticed these findings, the next challenge in this study was to apply the absorber, processed with the identified optimal T_{so} and T_{sub}, in a superstrate configuration solar cell with TiO₂ or CdS as the junction partner layer.

3.2. Bi₂S₃ device efficiency: analysis of the performance limitations

Based on the above analysis of the systematical structural changes in the Bi₂S₃ film growth depending on the CSS source and substrate deposition temperatures, we further analyzed how these structural changes correlate with the efficiencies of superstrate configuration glass/FTO/CdS/Bi₂S₃/Au and glass/FTO/TiO₂/Bi₂S₃/Au thin film solar cells. Fig. 7a show the schematic of the two device configurations

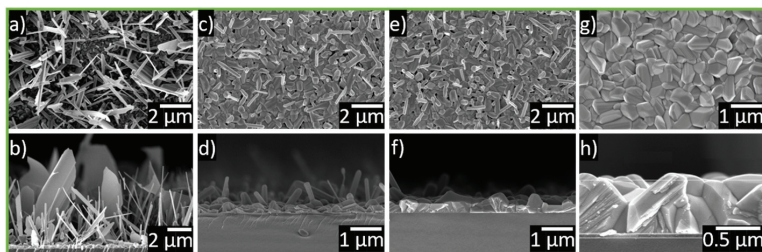


Fig. 5. (a, c, e, g) Top view and (b, d, f, h) cross-sectional SEM images of Bi₂S₃ films deposited onto a plain glass substrate at: (a,b) substrate temperature (T_{sub}) of 250 °C for 1 min deposition time; T_{sub} 450 °C at (c,d) 1 min, (e,f) 3 min, and (g,h) 5 min deposition time.

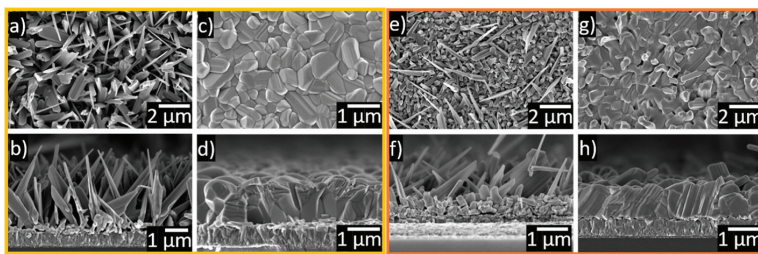


Fig. 6. (a, c, e, g) Top view and (b, d, f, h) cross-sectional SEM images of Bi_2S_3 films deposited onto (a–d) TiO_2 and (e–h) CdS substrates, at substrate temperature (T_{sub}) of (a–b, e–f) 250 °C and (c–d, g–h) 450 °C, deposition time is 1 min.

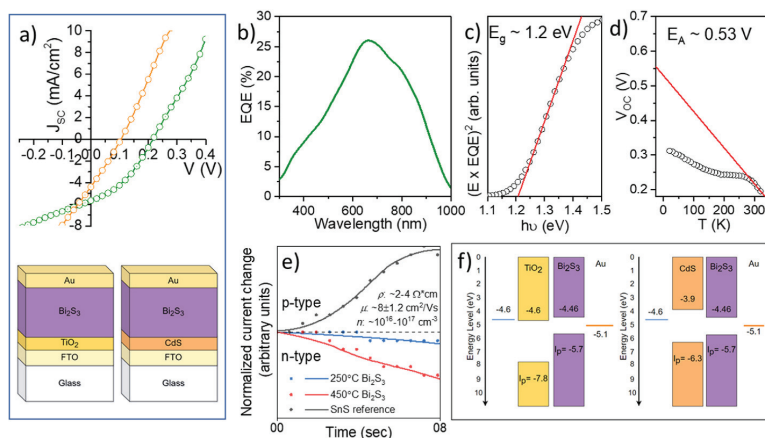


Fig. 7. a) Superstrate schematic configuration of the glass/FTO/ $\text{CdS}/\text{Bi}_2\text{S}_3/\text{Au}$ and glass/FTO/ $\text{TiO}_2/\text{Bi}_2\text{S}_3/\text{Au}$ thin film solar cells and representative J-V characteristics for the best devices (orange curve for $\text{CdS}/\text{Bi}_2\text{S}_3$, and green curve for $\text{TiO}_2/\text{Bi}_2\text{S}_3$). b) and c) Respective EQE spectral response and related modified EQE plot, giving a band gap estimation of 1.2 eV of Bi_2S_3 at RT. d) V_{OC} temperature dependence together with the extrapolation to 0 K for the estimation of the activation energy (E_A). e) hot-probe and relevant results of the Hall measurements of the carrier type and electron concentration in Bi_2S_3 thin film absorber. f) Band offsets with the estimation of the ionization energies for two configuration devices, measured via photoelectron emission spectroscopy method.

together with the representative J - V characteristics for the best devices, both of them processed with Bi_2S_3 absorber deposited at 450 °C. It can be seen that the $\text{TiO}_2/\text{Bi}_2\text{S}_3$ cell exhibit better efficiency compared to $\text{CdS}/\text{Bi}_2\text{S}_3$ device. A set of 5 cells (0.5 cm^2 contact area) were fabricated for each device structure, leading to an average device performance of $\eta \sim 0.1 \pm 0.05\%$ (with $V_{\text{OC}} \sim 90 \pm 10$ mV, $J_{\text{SC}} \sim 3.5 \pm 0.7$ mA/cm^2 , and $FF \sim 23.0 \pm 0.3\%$) and $\eta \sim 0.3 \pm 0.05\%$ (with $V_{\text{OC}} \sim 190 \pm 10$ mV, $J_{\text{SC}} \sim 4.6 \pm 0.8$ mA/cm^2 , and $FF \sim 32.0 \pm 0.3\%$) for $\text{CdS}/\text{Bi}_2\text{S}_3$ and $\text{TiO}_2/\text{Bi}_2\text{S}_3$, respectively. For the latest configuration, the highest achieved efficiency was $\eta \sim 0.45\%$, with $V_{\text{OC}} \sim 210$ mV, $J_{\text{SC}} \sim 5.7$ mA/cm^2 , and $FF \sim 38\%$. For both device configuration, processed with Bi_2S_3 at CSS substrate temperatures below 400 °C, the efficiencies tend to be zero. The EQE of the best device (Fig. 7b) shows quite modest response throughout the whole wavelength interval, in correlation with the representative J - V characteristics (Fig. 7a). The modified EQE plot (Fig. 7c) gave a band gap estimation of $E_g \sim 1.2$ eV for Bi_2S_3 at room temperature, in agreement with the values reported in the literature [37].

So far, these results indicate that the morphology of Bi_2S_3 has an impact on the cell performance, however, the modest $\text{TiO}_2/\text{Bi}_2\text{S}_3$ cell efficiency (which incorporates an absorber with larger and compact grains, Fig. 6d) clearly indicates that there are other factors which drastically affects the final cell performance. On one hand, the low EQE response suggests that the carrier collection at the contacts is well reduced. Moreover, it also indicates low carrier collection close to the buffer-absorber interface (i.e., high recombination velocity at the interface and small diffusion length of the minority carriers in bulk) [38]. The last argument is also supported by the activation energy value of $E_A \sim 0.53$ eV, obtained from V_{OC} temperature dependence (Fig. 7d).

This value is well below the bandgap energy, indicating that the interface recombination has a significant role in limiting the V_{OC} of these devices. On another hand, it is well known that the conductivity type and carrier concentration in the absorber, together with the buffer-absorber band offset also play a significant role in the formation of the heterojunction interface and resulted space charge region (SCR). The width of the SCR at the heterojunction interface depends on many factors, but among them, the carrier concentration in both, buffer and absorber layers have a key role. The conductivity type and carrier concentration of the Bi_2S_3 absorber layers deposited on glass substrates were analyzed by the hot-point probe and Hall measurements, respectively (Fig. 7e). For the hot probe analysis, SnS thin film deposited by CSS on the same glass substrates was used also as a good p-type reference [39]. Independent of the CSS deposition temperatures, the Bi_2S_3 absorber layers always showed n-type conductivity with an electron concentration of $n \sim 10^{16}$ – 10^{17} cm^{-3} and electron mobilities of $4.0 \pm 0.8 \text{ cm}^2/\text{Vs}$ and $8.0 \pm 1.2 \text{ cm}^2/\text{Vs}$, for the films deposited at $T_{\text{so}} 550$ °C and $T_{\text{sub}} 250$ °C–450 °C, respectively. These results imply that both $\text{CdS}/\text{Bi}_2\text{S}_3$, as well as $\text{TiO}_2/\text{Bi}_2\text{S}_3$, are described as an n-n isotype heterojunction. The high values of the electron density in the absorber imply that the SCR is very narrow and most likely extends into the buffer layer, at the heterojunction interface, leading to ineffective charge separation, and high recombination rates. All these effects justify the poor performance of the CdS and TiO_2 -based devices. In the case of both, n-n isotype and n-p heterojunctions, for the n-type layer, the electron density should be 1–2 orders of magnitude above the carrier concentration in the absorber material. This would allow an efficient charge separation and transport assuming the existence of a suitable 0.2–0.4 eV conduction band spike offset between the buffer and absorber layers [40]. In addition, the n-n

isotype heterojunction device will be very sensitive to the band offset and formation of the related interface defect state density. The ionization energy values for the constituent layers in the solar cell stack were obtained from photoelectron emission spectroscopy measurements. Fig. 7f shows the band energy diagrams of CdS/Bi₂S₃ and TiO₂/Bi₂S₃ solar cells with estimated values of the ionization energies. For the CdS/Bi₂S₃ device, the formation of a “spikelike” band offset can be assumed, as the conduction band minimum (CBM) of the CdS buffer layer lies above the CBM of the absorber [41]. In this case, the too-positive offset of the CdS CBM (~0.5 eV) creates a potential barrier for the excited electrons in the Bi₂S₃ absorber, opposing their drift into the buffer layer and thereby drastically lowering the J_{SC} and hence, the efficiency of device (Fig. 7a). In the case of TiO₂/Bi₂S₃ device, however, the formation of a “clifflike” offset can be distinguished (Fig. 7f) in which the CBM of the TiO₂ film lies below that of the absorber. For a such band alignment, the back-transfer carrier recombination at the main interface, in which the electrons in the TiO₂ film recombine with holes in the Bi₂S₃ absorber via interface states, is more likely. The latest phenomenon limits the built-in voltage of the heterojunction and hence the V_{OC} and efficiency of the cell.

The above solar cell results and related analysis indicate that the TiO₂/Bi₂S₃ device is described as n-n isotype heterojunction and among all the aforementioned limitations effects, the high electron concentration determined by the defects in the bulk of the absorber together with recombination at the main interface are the most detrimental. In this regard, temperature-dependence admittance spectroscopy can provide more insights on defect features in the Bi₂S₃ absorber. However, our attempts to perform such measurements failed, as for such a low-quality n-n type heterojunction it was difficult to detect the inflection frequency in the admittance spectrum. However, we succeeded to perform low-temperature dependence spectra, as described in the following 3.3 section.

3.3. Unveiling defects and possible recombination in Bi₂S₃ absorber from photoluminescence analysis

To explore the existence of possible defects in Bi₂S₃, low-temperature photoluminescence (PL) spectra were measured for Bi₂S₃ absorber layers deposited onto glass, CdS/FTO/glass, and TiO/FTO/glass stacks. It is worth mentioning that there are a very limited number of reports in the literature on PL studies of Bi₂S₃ thin films deposited by physical deposition techniques. As it has been more popular to synthesize Bi₂S₃ using chemical deposition methods, several reports employed room temperature PL analysis for Bi₂S₃ nanowires [42], nanoleafs [43], nanoparticles, and complex nanostructures [44,45], as well as for the Bi₂S₃ heterojunction-based structures for photocatalytic and hydrogen productions applications [46]. Related to Bi₂S₃ films processed by physical deposition methods, only two relatively recent studies by Haaf et al. [25] and by Jamali et al. [47] reported room temperature PL analysis. Employing confocal photoluminescence spectroscopy, Haaf et al. proved the advantages of the high-temperature deposition range for optical properties and therefore suggest, together with the results from both surface analysis and conductivity measurements, the preparation of solar cell structures at temperatures ≥ 240 °C during Bi₂S₃ deposition. Jamali et al. performed room temperature PL analysis for Bi₂S₃/SnS thin film heterojunction-based photodetector. Therein the authors assigned several two PL emissions with bismuth vacancy (V_{Bi}) and sulfur interstitials (S_i). However, in both aforementioned studies, the PL was not performed at low temperatures and hence, no in-depth analysis of possible defect-related transitions was discussed. Therefore, we aimed to perform a systematic analysis of low-temperature PL and temperature PL study in CSS Bi₂S₃ thin films and provide a correlation between defect features in the absorber and the performance of the solar cell device. For simplicity, the temperature dependence PL spectra of Bi₂S₃ deposited on glass, CdS/FTO/glass, and TiO/FTO/glass stacks are presented in Fig. S6, Supplementary material. Fig. 8a shows the PL

spectra measured at 100 K for the Bi₂S₃ deposited at 400 °C onto TiO₂/FTO substrate. For this specific configuration, the highest PL yield was obtained and therefore the analysis was focused on this sample but in general, the results can be extrapolated for the whole series of investigated structures. Looking at Fig. 8 (a) the broad PL band indicates to the presence of a high concentration of defects in the Bi₂S₃ absorber layer. The best fitting was achieved considering three bands labeled as B1 – main emission, at 1.13 eV, B2 – at lower energies, 0.86 eV, and B3 – at higher energies, 1.23 eV.

To further understand the origin of these three emissions, the displacement of the band's positions depending on the measurement temperature was analyzed. Fig. 8b–d shows this dependence for all three bands and it can be observed that all the bands follow almost the same trend with increasing temperature, distinguishing three regions: region–(I) low-temperature region, 10–75 K, in which the band position shifts towards lower energies; region–(II) between 75 K and 100 K, where the band position does not change; and region–(III) high-temperature region, 100–150 K, in which the band position shifts towards higher energies. Such behavior in the temperature dependence of band position has been observed in other materials [48] and indicates the implication of phenomena such as band-to-impurity transition in the presence of potential fluctuations in the materials and/or transitions within deep donor-deep acceptor (DD-DA) pairs.

To assign one of these models, each band (B1–B3) should be analyzed separately, including additional laser power dependence measurements. For the main B1, laser power dependence (Fig. 8e) shows a very small shift of about three meV per decade. Such a small shift is possible in the case of Deep Donor – Deep Acceptor (DD-DA) recombination. For shallow D–A pair it is expected a higher shift, of ~10 meV per decade, while for the band to impurity transition, even a higher shift is expected, ≥ 20 meV. The activation energy of $\sim 53.0 \pm 0.2$ meV was determined from the Arrhenius plot of the resulting integral intensities for B1. Similar activation energies around 50 mV were obtained for the B1 PL band of Bi₂S₃ deposited on glass and CdS/FTO/glass substrates, presented together with the respective temperature dependence PL spectra in Fig. S6, Supplementary material. If to assume the implication of potential fluctuation in the material, then the activation energy should be in the range of ~120 meV, so that to satisfy the correlation between band gap energy (~1.2 eV) and activation energy of the respective B1-related band emission. Here, this seems not to be the case, thus the DD-DA still remains the most probable recombination mechanism related to B1. In addition to this argument, the B1 band shape is quite symmetric which also excludes the implications of potential fluctuation. Related to B2 emission, its broadness and small intensity suggest that it is still related to deep defects, since it is still energetically far from the bandgap energy, about 350–370 meV from the bandgap energy. Looking at the B3 emission, it has a very small intensity and it is more prominent at higher temperatures. Considering its position at 1.23 eV, it could be related to band-to-band emission.

Coming back to the analysis of B1 emission, a natural question that arises then is how the presence of DD-DA recombination correlates with the electrical properties of Bi₂S₃ presented above. The obtained relatively high electron concentration of 10^{16} – 10^{17} cm⁻³ clearly indicates to the presence of shallow donors in Bi₂S₃ absorber films. A pertinent answer would be that this DD-DA involved in the B1 emission is a neutral complex that does not have an impact on the electrical properties. The initial donor is deep and the initial acceptor is also deep, and only for the closely separated DD-DA pairs the energy is decreasing, resulting in a rather small activation energy obtained in Fig. 8f. As a rule of thumb, this activation energy (~53 meV) is attributed to a shallow acceptor, as the PL temperature quenching in most of the materials is related to the acceptor level. From a theoretical perspective, the first-principles DFT calculations provide a larger variety of defects in Bi₂S₃ [37]. The donor defects such as vacancies of sulfur (V_S) have much lower formation energies, under both, Bi-rich and S-poor or under the Bi-poor and S-rich conditions [37]. Thus, n-type conductivity and higher

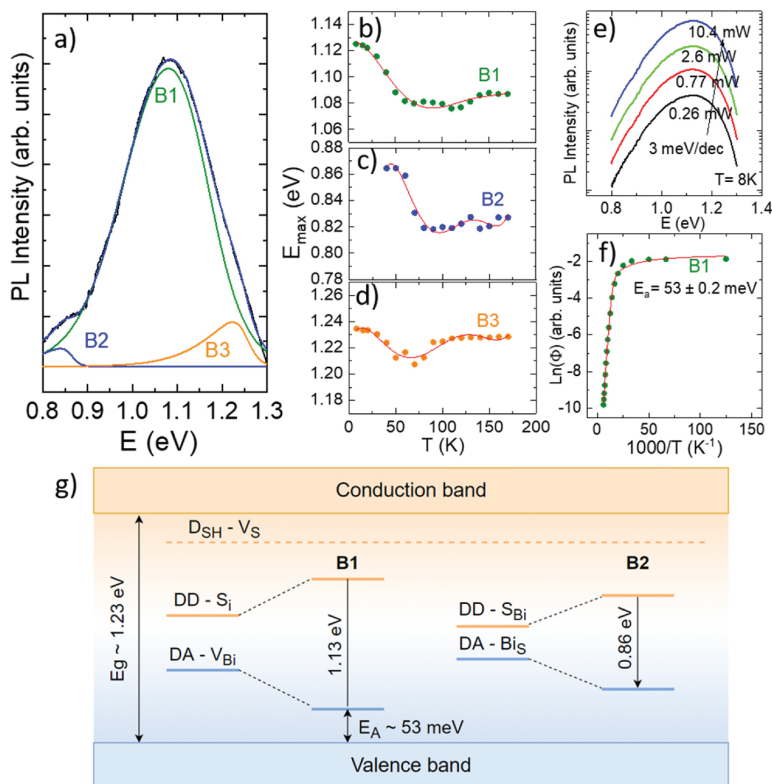


Fig. 8. (a) Photoluminescence spectrum at 100 K, for Bi_2S_3 absorber layer deposited on top of $\text{TiO}_2/\text{FTO}/\text{glass}$ substrate; the best fitting was achieved with three bands: B1 at 1.13 eV (green), B2 at 0.86 eV (blue), and B3 at 1.23 eV (orange). b-d) Shift of each band position depending of the measurement temperature. e) Laser power dependence of the low-temperature B1 PL band, showing a shift of ~ 3 meV per decade. f) Arrhenius plots of the integral intensity of the B1 PL band with the fitting result. g) Proposed Deep-Donor to Deep Acceptor (DD-DA) recombination model for Bi_2S_3 absorber films at 8 K. The $D_{\text{SH}} - V_{\text{S}}$ label in the diagram designates the sulfur vacancy shallow donor.

electron concentration are usually expected in Bi_2S_3 . Interestingly, most of the intrinsic point defects act as donors, even the anion interstitial sulfur (S_i), which is usually an acceptor in other chalcogenide semiconductors [39], acts as a donor. Only vacancies of bismuth (V_{Bi}) and antisite Bi_{S} act as acceptor defects [37], but both these defects are very deep (high) within the bandgap, close to the conduction band minimum so that their ionization does not occur effectively in order to generate higher concentration hole carriers. Thus, this defect configuration makes p-type doping in Bi_2S_3 quite challenging. Based on the above PL analysis and considering the aforementioned possible formation of defects in Bi_2S_3 , a model of the DD-DA recombination mechanism is proposed in Fig. 8g. For the B1 emission, the DD and DA were assigned to S_i and V_{Bi} , respectively while the B2 band was attributed to the second DD-DA pair (next closest distance) implying a deeper donor and acceptor of S_{Bi} and Bi_{S} , respectively. At the same time, it is also possible that the B2 band is related to the same the DD-DA pair as for the B1 band (i.e. the initial positions of defect levels will be the same), but with a larger distance between DD and DA in the lattice, resulting in slightly deeper energy levels for the DD-DA pair. Such high concentration of defects involving deep pair complex configuration, explains why the efficiencies of the respective isotype heterojunction $\text{CdS}/\text{Bi}_2\text{S}_3$ and $\text{TiO}_2/\text{Bi}_2\text{S}_3$ solar cells are so modest. These results are good agreement with the first-principle theoretical predictions [37] in which the high concentration of point defects (such as Bi_{S} , V_{S} , or S_{Bi} , S_i) in Bi_2S_3 can produce deep levels in the band gap and act as electron-hole recombination centers, decreasing the lifetime of the minority carriers and the efficiency of the solar cell. A carrier lifetime in the orders of 10–50 ps [37] would be even more critical for a n-n type heterojunction with a very weak electric field. Thus, the development of p-n heterojunction Bi_2S_3 solar cells [15] can facilitate the electron-hole separation by the

build in electric field and thus increase the carrier lifetime as well as the performance of the solar cell device. Implementation of possible processing strategies such as p-type doping of the absorber together with identification of alternative optimal heterojunction partner layer with suitable band offset remains largely unexplored approaches for this material and could offer new perspectives to improve the performance of Bi_2S_3 thin film solar cells.

4. Conclusions

In conclusion, we systematically studied the impact of CSS processing conditions on the properties of Bi_2S_3 thin film absorber deposited on various substrates and analyzed the interrelation between the changes in the absorber properties and device performance. The source temperature of 550 °C and substrate temperature of 400–450 °C were identified as optimal temperatures which allowed a reasonable deposition rate (~ 0.5 – $0.8 \mu\text{m}/\text{min}$) and fabrication of uniform Bi_2S_3 films with a suitable (hkl , $l = 1$) orientation independent whether the deposition was performed on either plain glass, TiO_2 or CdS as substrate. At T_{so} below the optimal one, independent of the applied substrate temperatures, the absorber grains were predominantly oriented along (hkl , $l = 0$), while a high amount of amorphous phase was observed in Bi_2S_3 film grown at source temperature 450 °C. 600 °C source temperature was identified as a critical temperature, generating conditions for sulfur loss in the Bi_2S_3 system with the formation of separated metallic bismuth and Bi_2S_3 phases. For the source temperature 550 °C, independent of the substrate temperature and the used substrate for the deposition of Bi_2S_3 films, Raman spectra showed similar vibrational modes, which correspond to the pure Bi_2S_3 phase. For the first time, a proof of concept of 0.45% efficient solar cells incorporating CSS Bi_2S_3 absorber layer is

demonstrated and an in-depth analysis of the interrelation between grain structure, interface recombination, and device performance is provided. Independent of the CSS deposition temperatures, the Bi₂S₃ absorber layers always showed n-type conductivity with an electron concentration of $n \sim 10^{16}$ – 10^{17} cm⁻³ and electron mobilities of 4.0 ± 0.8 cm² V⁻¹ s⁻¹ and 8.0 ± 1.2 cm² V⁻¹ s⁻¹, for Bi₂S₃ deposited at 250 °C and 450 °C, respectively. These results imply that both CdS/Bi₂S₃, as well as TiO₂/Bi₂S₃, are described as an n-n isotype heterojunction in which the space charge region is very narrow and most likely extends into the buffer layer, at the heterojunction interface, leading to ineffective charge separation, and high recombination rates. *V_{OC}*-*T* analysis of the device indicated that the interface recombination is one of the major limitations in the efficiency of the solar cell. The analysis of energy level alignment via photoelectron emission spectroscopy technique suggests the formation of a “spikelike” band alignment and a “clifflike” offset for CdS/Bi₂S₃ and TiO₂/Bi₂S₃ devices, respectively. Such energy level alignment implies limitations in the device performance due to a potential barrier and back-transfer carrier recombination at the main interface. Low-temperature dependence PL analysis shows the presence of three emissions bands: B1 at 1.13 eV, B2 at 0.86 eV, and B3 at 1.23 eV. Based on the temperature-dependent shift of band position and the activation energy calculated out of the Arrhenius plot, the Deep Donor to Deep Acceptor (DD-DA) recombination model for Bi₂S₃ absorber films was proposed. These results so far indicate the severe limitations of the Bi₂S₃-based n-n isotype heterojunction devices with the main limitation of reduced carrier collection [37] due to the very weak built-in electric field at n-n heterojunction interface. In this regard, the implementation of alloying between Bi- and Sb-chalcogenides shows promising results from the side of the material development [49,50]. In addition, p-type doping of Bi₂S₃ remains largely unexplored [37] and research efforts for the development of p-n heterojunction Bi₂S₃ solar cells [15] can facilitate the electron-hole separation by the built-in electric field and thus increase the carrier lifetime and the performance of this emerging solar cell device.

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Intellectual property

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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We confirm that the manuscript has been read and approved by all named authors.

We confirm that the order of authors listed in the manuscript has been approved by all named authors.

CRediT authorship contribution statement

M. Koltsov: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **S.V. Gopi:** Visualization, Methodology, Investigation. **T. Raadik:** Writing – review & editing, Investigation, Formal analysis. **J. Krustok:** Writing – review & editing, Validation, Formal analysis. **R. Josepson:** Investigation, Formal analysis. **R. Grzibovskis:** Investigation, Formal analysis. **A. Vembris:** Investigation, Formal analysis. **N. Spalatu:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, 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

No data was used for the research described in the article.

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Appendix A. Supplementary data

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Appendix 2

Publication II

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Composition-tunable ($\text{Sb}_x\text{Bi}_{1-x}$) $_2\text{S}_3$ solid-solution thin films via close-spaced sublimation

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ABSTRACT

Alloying strategies in Bi- and Sb-based chalcogenide absorbers remain largely unexplored for close-spaced sublimation (CSS), despite their potential for tailoring bandgap and electronic properties. Here, we report for the first time the development of ($\text{Sb}_x\text{Bi}_{1-x}$) $_2\text{S}_3$ solid solutions by CSS, spanning a holistic processing framework, from ingot synthesis and thermodynamic analysis of the vapor-phase composition to thin-film absorber validation and proof-of-concept device demonstration. Composition-matched ($\text{Sb}_x\text{Bi}_{1-x}$) $_2\text{S}_3$ source materials ($x = 0.1\text{--}0.9$) were synthesized and systematically screened by CSS, enabling the establishment of composition-dependent growth regimes that yield dense, homogeneous absorber layers across the entire solid-solution range. Structural characterization confirms the formation of single-phase orthorhombic solid solutions with continuous lattice evolution. Optical analysis reveals systematic bandgap tunability, from ~ 1.3 eV to ~ 1.7 eV, in line with theoretical predictions. Low-temperature photoluminescence measurements, reported here for the first time for CSS-grown ($\text{Sb}_x\text{Bi}_{1-x}$) $_2\text{S}_3$ films, suggest that radiative recombination involves localized and exciton-assisted processes. Finally, a proof-of-concept solar cell employing a ($\text{Sb}_{0.9}\text{Bi}_{0.1}$) $_2\text{S}_3$ absorber is demonstrated, validating the functionality of CSS-deposited solid-solution absorbers and highlighting their potential for customized PV applications.

1. Introduction

The transition toward resource-efficient and sustainable energy technologies requires accelerated development of photovoltaic (PV) materials and device concepts that extend beyond the performance boundaries and application scope of established Si-based technologies. At this stage, emerging PV absorbers are expected not only to approach competitive efficiencies but also to rely on earth-abundant, environmentally benign elements, while offering new degrees of freedom in optoelectronic property design to address applications such as tandem photovoltaics, indoor PV, and extended green, responsible optoelectronic applications [1,2].

Within this context, Sb- and Bi-based chalcogenides have emerged as a promising class of absorber materials. Compounds such as Sb_2S_3 ,

Sb_2Se_3 , $\text{Sb}_2(\text{S,Se})_3$, Bi_2S_3 , and related ternary or multinary systems combine high absorption coefficients ($\sim 10^5 \text{ cm}^{-1}$), tunable bandgaps in the 1.1–1.8 eV range, and intrinsic chemical stability [3–6]. Over the past decade, substantial progress in device performance has been achieved, with reported power conversion efficiencies (PCEs) reaching $\sim 8.2\%$ for Sb_2S_3 [7], $\sim 10.6\%$ for Sb_2Se_3 [8], $\sim 10.7\%$ for $\text{Sb}_2(\text{S,Se})_3$ [9], and $\sim 10.8\%$ for AgBiS_2 -based devices [10], enabled mainly by advances in thin-film growth control, defect management, and interface engineering. Recent research efforts on Sb- and Bi-based chalcogenide absorbers have primarily focused on optimizing deposition strategies to promote favorable ribbon or columnar grain orientation and on fine-tuning heterointerfaces with electron transport layers (ETLs) such as CdS or TiO_2 to improve charge separation and collection [11–15]. In parallel, targeted defect-engineering approaches—such as controlled

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doping or cation disorder engineering in related chalcogenide systems—have demonstrated the potential to mitigate recombination losses and enhance open-circuit voltage [16,17]. However, despite these advances, alloying strategies in Sb- and Bi-based sulfides remain surprisingly underexplored, particularly in the context of solid-solution thin films prepared by physical vapor deposition methods.

From a materials perspective, the Bi_2S_3 – Sb_2S_3 system represents an ideal platform for alloy engineering. Sb_2S_3 and Bi_2S_3 share the same orthorhombic crystal structure ($Pnma$) [18–20], contain the same chalcogen anion, and feature cations of comparable ionic radii, resulting in a lattice mismatch below $\sim 3\%$. As a consequence, they exhibit a high degree of mutual solubility [21,22], enabling the formation of continuous $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions across the full compositional range. At the same time, their optoelectronic properties differ markedly: Sb_2S_3 exhibits a wider bandgap (~ 1.7 eV) and high resistivity (often $>10^6$ $\Omega\cdot\text{cm}$), commonly described as intrinsically self-compensated with a tendency toward p-type conductivity [11], whereas Bi_2S_3 shows a narrower bandgap (~ 1.3 eV), n-type conductivity, and significantly higher electron concentrations (typically $\sim 10^{17}$ $1/\text{cm}^3$) [23]. This intrinsic contrast naturally motivates alloying as a route to continuously tune bandgap, carrier density, and transport behavior within a single absorber system.

Historically, $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions were first investigated in mineralogy and high-temperature bulk synthesis, where compositional trends in lattice parameters and melting behavior were established [24, 25]. Subsequent studies explored chemically deposited thin films and nanostructures, primarily focusing on structural and optical properties, including composition-dependent bandgap variation.

In terms of applications, these solid solutions have been examined mainly for energy storage and photocatalysis [26–29], while PV-related studies have largely been limited to low-level Bi doping of Sb_2S_3 , typically below a few atomic percent [30]. Importantly, systematic investigations of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution thin films deposited by physical vapor deposition—and in particular by close-spaced sublimation (CSS)—are essentially absent, as highlighted by the literature survey in Fig. 1, which reveals that existing studies are dominated by chemical synthesis routes and largely limited to bulk materials or nanostructures rather than thin-film absorbers. CSS is a well-established, industrially relevant deposition technique for chalcogenide absorbers (such as CdTe) [31,32], offering high material utilization, compatibility with large-area processing, and precise control over source and substrate temperatures. While close-spaced sublimation has been optimized to a reasonable extent for binary Sb- and Bi-based chalcogenide absorbers,

enabling the formation of compact films and solar cell efficiencies approaching those achieved by chemically processed counterparts, its application remains limited to a small number of reports, particularly for Bi_2S_3 , where only a few CSS studies have been published to date [6]. More importantly, the potential of CSS for composition-tunable solid-solution systems remains largely unexplored, especially with respect to vapor-phase equilibrium calculations, composition-dependent growth regimes, and absorber validation in PV devices (Fig. 2).

In this context, the aim of the present study is to develop, for the first time, a comprehensive CSS-based framework for composition-tunable $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution thin films, spanning the full workflow from ingot synthesis and thermodynamic analysis of the vapor phase to thin-film growth screening and proof-of-concept device demonstration. The novelty of this work lies in the systematic, composition-resolved identification of CSS growth regimes, enabling the reproducible fabrication of dense, homogeneous absorber layers across the entire Bi_2S_3 – Sb_2S_3 solid-solution range.

Using this approach, we establish composition-dependent optimal growth windows, demonstrate continuous tuning of structural, optical, and electrical properties—including bandgap (~ 1.3 – 1.7 eV) and carrier density spanning more than two orders of magnitude—and provide the first low-temperature photoluminescence insights for CSS-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ films. Finally, the PV functionality of the solid-solution absorbers is validated through a proof-of-concept solar cell employing a $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ absorber, demonstrating the viability of this materials platform for customized PV and related optoelectronic applications.

2. Experimental

$(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions were prepared from Sb_2S_3 and Bi_2S_3 lump precursors (ThermoElectric, 5 N purity). Both precursors were finely ground with a mortar and pestle, then mixed with molar ratios of 10.0%, 33.3%, 50.0%, 66.6%, and 90.0% of Sb_2S_3 in Bi_2S_3 , respectively.

2.1. Preparation of solid solutions

At the solid solution preparation step, the mixes were placed into the quartz ampoules, vacuumized to a pressure of ~ 1 Pa, and sealed using an acetylene blowtorch. Further, ampoules were put into the tubular furnace for 24 h at 800°C , above both melting points of Sb_2S_3 (550°C) and Bi_2S_3 (775°C), with the heating ramp of $10^\circ\text{C}/\text{min}$. The slow cooling was performed with the initial ramp of 8 – $9^\circ\text{C}/\text{min}$ and the main ramp of 2 – $3^\circ\text{C}/\text{min}$ down to room temperature. In this way, both

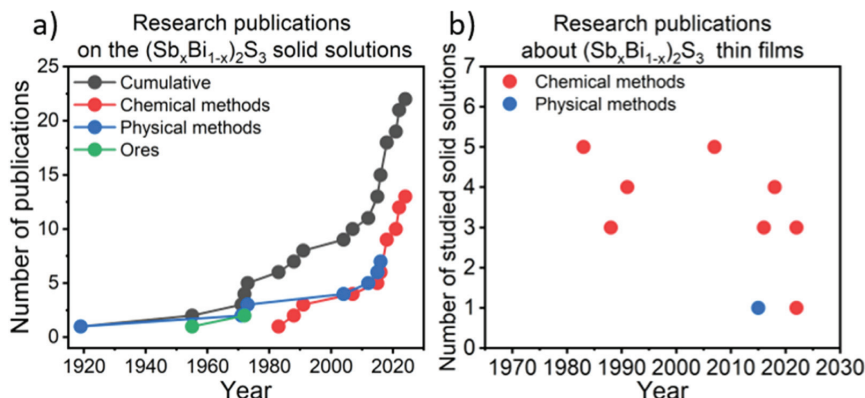


Fig. 1. Overview of the current research efforts on the development of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions based on a survey of the published literature. (a) Cumulative number of publications reporting $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions, categorized by chemical synthesis routes, physical deposition methods, and mineral (ore-based) studies. (b) Publications specifically addressing deposition of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, highlighting the scarcity of solid-solution thin-film studies and the dominance of chemical processing routes, with very limited reports employing physical vapor deposition methods.

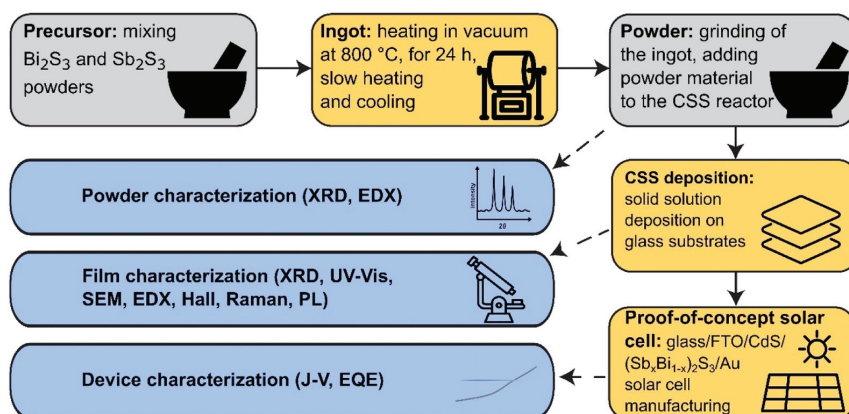


Fig. 2. The schematically depicted main steps of the sample preparation procedure.

components of the solid solution went through the liquid phase for better intermixing. Then, the resulting ingots were ground into powders for the following characterization and thin film deposition.

2.2. Thin film preparation

Thin films were deposited on plain glass substrate (Sigma Aldrich Glass/FTO substrates, non-coated side) by CSS using a custom-made reactor [6,33,34]. 0.03 g of the powder obtained from the ingots was loaded into the reactor. The main parameters of CSS deposition are substrate temperature, source temperature [35], time of deposition, as well as multiple other parameters (spacing (the distance between the source and the substrate), ambient gas, ambient gas pressure, cooling rate, source material fraction, substrate roughness, etc.). In this work, some of the parameters were standardized by design: (i) CSS reactors had a constant distance between the source and substrate; (ii) deposition lasted in a vacuum (pressure around 3×10^{-6} Torr or 0.0004 Pa), with no ambient gas involved in the deposition. The deposition conditions (T_{sub} , T_{so} , time), as the main variables, are described in a corresponding section.

2.3. Material characterization

X-ray diffraction (XRD) data were acquired using a Rigaku Ultima IV diffractometer, utilizing Cu K α radiation ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA), and processed with PDXL2 software. The surface and cross-sectional imagery of the thin films were captured using a Zeiss HR-SEM MERLIN equipped with a GEMINI II column. The SEM setup was coupled with the Energy Dispersive X-ray Spectroscopy (EDX), used for compositional analysis of the thin films, both in cross-section and top surface.

Raman scattering analysis of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions was performed using an FHR 640 monochromator from Horiba, coupled with a CCD detector. A solid-state laser with a 532 nm emission line was used as an excitation source, setting the power at $\sim 1 \text{ mW}$ over a $\sim 70 \text{ }\mu\text{m}$ diameter spot. The measurements were performed in a backscattering configuration through a special probe designed in IREC. Up to 16 points were assessed in each sample, revealing information about lateral homogeneity in the thin films. All spectra were normalized to the position of the main peak of monocrystalline Si by imposing its peak to 520 cm^{-1} . Absorbance spectra of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films were measured using a Jasco V 730 spectrometer in the range of 190–800 nm at room temperature. Resistivity and charge density were obtained via Van der Pauw/Hall measurement using the Hall and Van der Pauw Controller H-50 from MMR Technologies. For the materials, whose resistivity was too

high to be measured reliably via the H-50 (with a possibility to perform accurate measurements for carrier density and mobility for resistivity values up to $10^6\text{--}10^7 \text{ Ohm}\cdot\text{cm}$). The setup has the capability to measure the linearity of the contact, and for each measurement, it provides the optimal currents to perform the measurements.

PL characterization was conducted using two lasers - DPSS 266 nm pulsed laser (SNU-20F-100, Teem PhotonicsTM) with repetition rate 19 kHz, constant pulse width range (FWHM) 0.6 ns, laser spot diameter = 0.32 mm; and DPSS 532 nm CW laser (MGL-III-532, CNL) with laser spot diameter = 0.21 mm. In both cases, the intensity was varied using a neutral density gradient filter. PL detection was done with a conventional lock-in system - thermoelectrically cooled InGaAs (IGA-030 TE2-H, EOS) photodetector (set on glass - 266 nm measurements) and liquid nitrogen cooled InGaAs (IGA2.2-010-LN, EOS) photodetector (set on glass - 532 nm measurements, set on CdS - 266 nm and 532 nm measurements). For temperature control, samples were mounted on the cold finger of a closed-cycle He cryostat (JANIS) coupled with a temperature controller (Lakeshore).

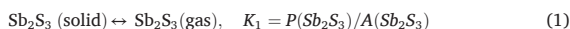
2.4. Solar cell characterization

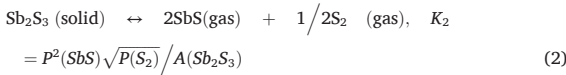
The solar cell properties were characterized by the JV measurement using AUTOLAB PGSTAT 30 and Oriel class A solar simulator 91159 A ($100 \text{ mW}/\text{cm}^2$, AM1.5 G). The External Quantum Efficiency (EQE) measurements were conducted on the solar cells in the 300–900 nm wavelength range using Newport 300 W Xenon lamp 69911 as a light source, a Newport Cornerstone 260 monochromator, and a Merlin Si-calibrated detector.

3. Results and discussion

3.1. Thermodynamic considerations of the $\text{Bi}_2\text{S}_3\text{--Sb}_2\text{S}_3$ system

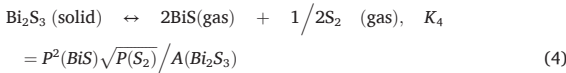
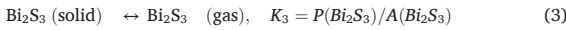
Understanding the thermodynamic parameters influencing the growth of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ ingots and thin films is essential for optimizing their composition and phase stability during synthesis. However, to date, thermodynamic analyses of vapor-phase equilibrium and growth behavior have been largely limited to binary Sb_2S_3 [36] and Bi_2S_3 [37] systems and have not been systematically extended to composition-tunable solid-solution absorbers processed by CSS. The composition of the vapor phase can be calculated using the thermodynamic principle of minimum Gibbs energy [38,39]. The main evaporation reactions of Sb_2S_3 can be written as follows:





where all pressures (P) are expressed in atmospheres (atm), $A(\text{Sb}_2\text{S}_3)$ is activity of Sb_2S_3 , and K_p are equilibrium constants of the corresponding reactions, which can be calculated using thermodynamic data of the reaction participants. Vapors of Sb_2S_3 and SbS can dissociate, causing the appearance of gaseous $(\text{SbS})_2$, $(\text{SbS})_3$, $(\text{SbS})_4$, Sb_2S_4 , Sb_3S_2 , Sb_4S_3 , Sb_4 , Sb_3 , Sb_2 , and Sb .

Similar evaporation reactions of Bi_2S_3 can be written as follows:



The gaseous Bi_2S_3 and BiS can also dissociate, generating $(\text{BiS})_2$, Bi_4 , Bi_3 , Bi_2 , and Bi . Vapors of $(\text{BiS})_3$, $(\text{BiS})_4$, Bi_2S_4 , Bi_3S_2 , and Bi_4S_3 are not stable.

The constancy of Bi, Sb, and S atoms in a solid-vapor system must also be considered using the corresponding equation for pressures P :

$$\sum_i a_i P_i^{\text{Bi}} + \sum_i b_i P_i^{\text{Sb}} = \frac{2}{3} \sum_i c_i P_i^{\text{S}} \quad (5)$$

where a_i (b_i , c_i) is the number of Bi (Sb, S) atoms in the Bi-related (Sb-, S-) gaseous species; the summation i is carried out over all gaseous substances. The joint calculation of equations for all K_p values (Eqs. 1–4, etc.), considering constancy of Bi, Sb, and S (Eq. 5), gives the

composition of vapor phase over $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid phase. In this case, the theory of ideal solid phase is assumed, when the activities A of solution components (Bi_2S_3 , Sb_2S_3) are equal to their molar fractions [38]. Thermodynamic data for Sb sulfides can be found in Ref. [40] for Bi sulfides, and metal vapors can be found in Ref. [41]. Examples of such thermodynamic calculations were described in previous works [42,43].

The temperature dependences of the calculated vapor phase composition over $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid phase (where $x = 0, 0.1, 0.5$, and 0.9), calculated from the Eqs. 1–5, are shown in Fig. 3. The main components of the gaseous medium over Bi_2S_3 are BiS and S_2 , with pressures of 4×10^{-10} and 2×10^{-10} atm, respectively, at 400°C . Bi_2 (4×10^{-11}) and Bi (6×10^{-11} atm at 400°C) vapors are less significant. Since the pressures of secondary gaseous substances such as Bi_2S_3 (6×10^{-17}), $(\text{BiS})_2$ (8×10^{-15}), Bi_4 (2×10^{-13}), and Bi_3 (4×10^{-15} atm at 400°C) are negligible, they are not shown.

The presence of Sb_2S_3 in the solid phase causes an increase in S_2 pressure, appearance of Sb_2S_3 (1×10^{-9}), SbS (4×10^{-10}), Sb_4 (8×10^{-10}), and Sb_3S_2 (2×10^{-10} atm at 400°C and $x = 0.5$) vapors, as well as a decrease in the pressure of Bi-related species for any of the temperatures under investigation. The pressures of $(\text{SbS})_2$ (4×10^{-12}), $(\text{SbS})_3$ (3×10^{-15}), $(\text{SbS})_4$ (2×10^{-15}), Sb_2S_4 (1×10^{-11}), Sb_4S_3 (3×10^{-14}), Sb_3 (5×10^{-14}), Sb_2 (2×10^{-11}), and Sb (8×10^{-15} atm at 400°C and $x = 0.5$) are negligible; they are not shown. The calculated temperature dependences are monotonic; the total pressure increases exponentially, but the fractions of various substances are almost constant or change relatively slowly. At relatively high temperatures ($T > 500^\circ\text{C}$), Bi_2S_3 can partially dissociate to S_2 vapor and Bi-S solid phase with various activities [44]. The present calculation results correspond to the initial stage of evaporation. The calculated total pressure (P_{total}) of Sb-related species is one order of magnitude higher

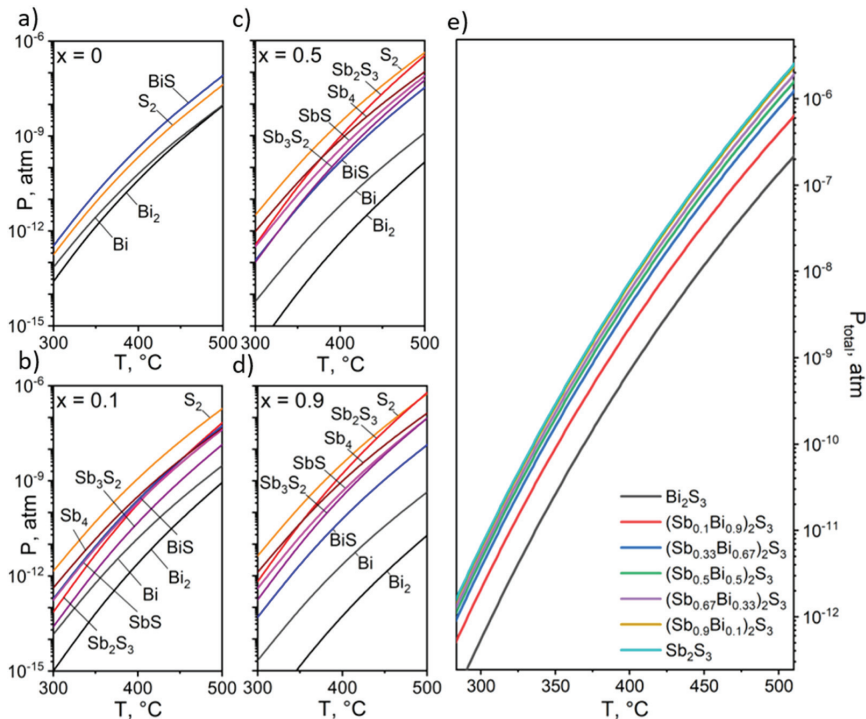


Fig. 3. Thermodynamic calculations of temperature-dependent vapor composition (main components) over $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid phase in the initial evaporation stage for (a) $x = 0$ (Bi_2S_3), (b) $x = 0.1$ ($(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$), (c) $x = 0.5$ ($(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$), and (d) $x = 0.9$ ($(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ solid phase; e) the temperature-dependent partial pressure of the gaseous phases for different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems.

than that of Bi-related species ($x \sim 0.5$).

This effect is consistent with a higher volatility of Sb_2S_3 (thus, a necessity of short deposition times for Sb_2S_3 , as established in the experiment). At the same time, the surface of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ during evaporation is quickly enriched by Bi, the activity of Bi_2S_3 (Sb_2S_3) components of the system increases (decreases). The equilibrium composition of the surface should correspond to the equality: flow (Bi atoms) / flow (Sb atoms) = Bi / Sb ratio in the solid solution. This well-known effect was observed for example in $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ single crystal growth [45].

The influence of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid phase composition on the vapor phase in equilibrium state at various temperatures is shown in Fig. 4. It can be seen that at high temperatures (at 500 °C and above) an elevated content of Sb_2S_3 vapors, S_2 and Bi-related species (mostly BiS), can be generated above the Sb-rich solid phase. The domination of Sb_2S_3 vapors above the solid Sb_2S_3 should be present at all temperatures (300 – 600 °C). At low Sb content in the solid phase ($x \leq 0.5$) and temperatures 400 – 600 °C, among all the Sb-related species, SbS vapors should dominate. At the lowest temperatures (300 °C) domination of the Sb_4 vapors is expected. Thus, the thermodynamic calculation shows that the main evaporation reaction for Bi_2S_3 itself and as a part of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems is related to BiS and S_2 vapors (Eq. 4). For Sb_2S_3 it is related (i) to SbS and S_2 vapors (Eq. 2) at moderate temperatures and low Sb content in the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ system, and (ii) to Sb_2S_3 vapors (Eq. 1) at high temperatures and high Sb content.

The deposition of Bi_2S_3 occurs at a relatively low vapor supersaturation ($P_{\text{total}}(\text{material source}) / P_{\text{total}}(\text{growing film})$) of about 6. As shown above, in the case of low Sb content in solid phase, the main evaporation reaction for Sb_2S_3 is similar; it is related to SbS and S_2 vapors. As a consequence, the optimal growth conditions for Bi-rich systems are expected to be close to those of Bi_2S_3 . The deposition of Sb_2S_3 films occurs at relatively high vapor supersaturation (of about 10^5). Since the main evaporation reaction for Sb-rich systems is similar, being related to Sb_2S_3 vapor, the deposition of continuous and dense $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films is also expected at very high vapor supersaturation. At the same time, for intermediate values of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ composition, the film growth should be determined by intermediate values of supersaturation.

Thus, in accordance with the above thermodynamic estimation of vapor phase composition over $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, the main evaporation reaction for Bi_2S_3 and Bi-rich solid phases is based on BiS (SbS) and S_2 vapors (Eqs. 2, 4), while the sublimation of Sb_2S_3 and Sb-rich solid phases occurs mostly congruently with participation of Sb_2S_3 (Eq. 1). These two evaporation mechanisms have various enthalpies, number of participated molecules, as well as molecular mass and growth rate.

Three-molecular reactions (Eqs. 2, 4) require slower deposition rates and consequently lower supersaturation for several molecules of the evaporation products to restructure on the substrate to form $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ crystals. The simplest one-molecular congruent evaporation (Eq. 1) has no this limitation; the deposition of Sb-rich systems is limited mostly by re-evaporation. The parameters above (partial pressures, supersaturation values) are expected to have a significant impact on identifying the optimal CSS processing conditions for the deposition of continuous and dense films. Thus, as a next approach, the focus was set on identifying suitable CSS deposition parameters to develop continuous, uniform thin films on glass substrates.

3.2. Synthesis and compositional control of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ source materials

As a first step towards the development of solid solutions and thin films, EDX analysis of the synthesized ingots of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ was performed to evaluate the effectiveness of the alloying process and ensure that the elemental composition of the ingot material aligns with the initial powder mixture. This step is critical to confirm the stoichiometric consistency and homogeneity of the source material before proceeding with thin-film fabrication via close-spaced sublimation.

Figs. 5a and 5b show the EDX results with the elemental composition of the initial Sb_2S_3 - Bi_2S_3 powder mixture and ingots, respectively. EDX analysis of the ingots (Fig. 5b) reveals that the obtained ingot alloys exhibit elemental composition and stoichiometry within a $\sim 3.5\text{at}\%$ margin from the initial Sb_2S_3 - Bi_2S_3 powder mixture, aligning very well with the targeted values. Considering the above (Figs. 3 and 4) aspects on the composition of the vapor phase at various temperatures and estimated sublimation mechanisms for both Sb-rich and Bi-rich $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, it is expected that optimal CSS deposition conditions will enable the fabrication of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ films with elemental compositions closely matching those of the ingot source material. Therefore, in the next step, we systematically screened the deposition parameters – such as source temperature, substrate temperature, and deposition rate – for the growth of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ films by CSS.

3.3. Composition-dependent CSS growth regimes of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films

The key target was to develop an optimized CSS processing protocol for depositing $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films with a columnar, sintered-grain morphology. As highlighted earlier, such absorber morphology is crucial for efficient charge transport in the thin-film solar cells. For this purpose, the CSS source and substrate temperatures (T_{so} , T_{sub}) were

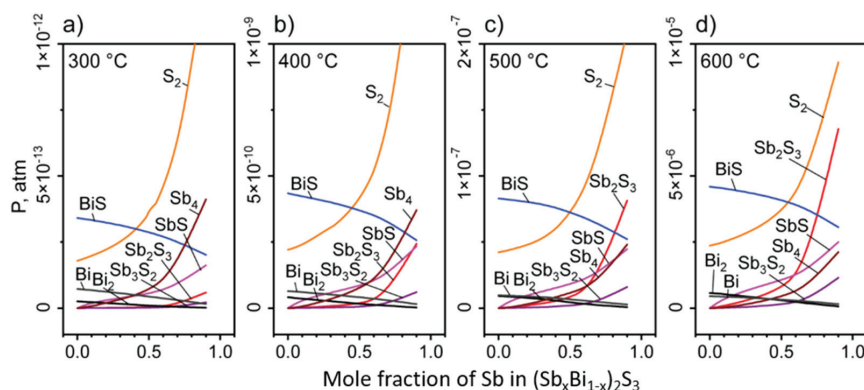


Fig. 4. Influence of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ composition on the vapor pressure of different species at indicated temperatures (equilibrium state) – (a) 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C.

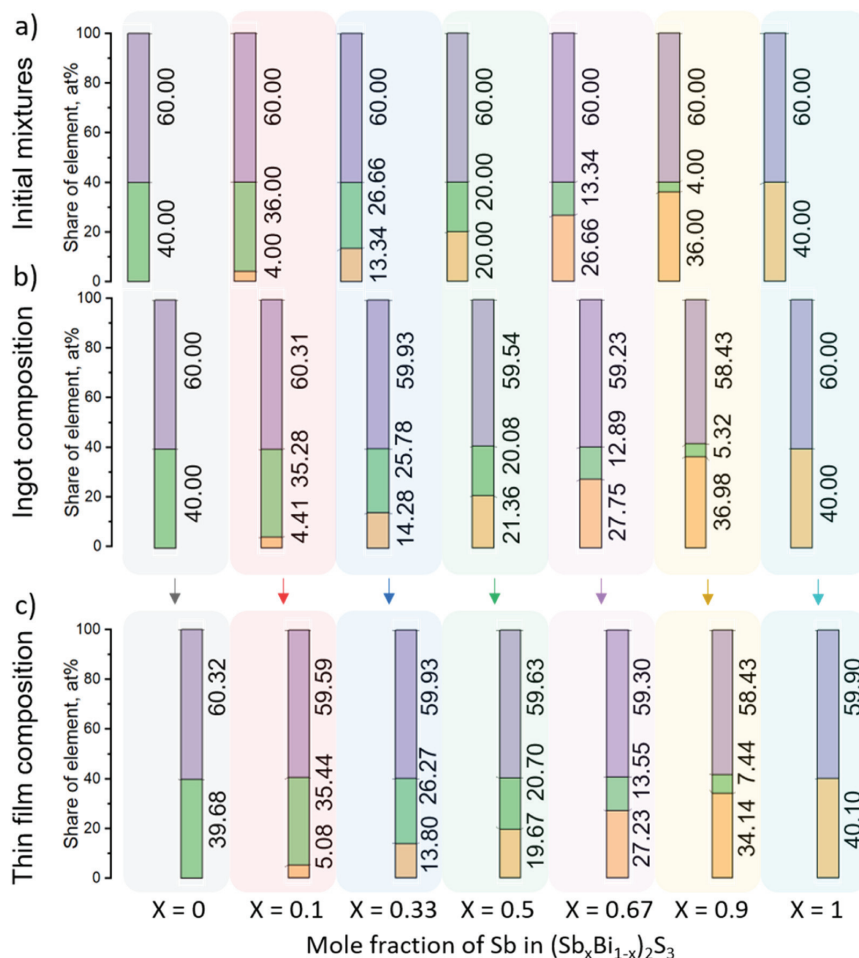


Fig. 5. Elemental compositions of (a) initial Bi_2S_3 - Sb_2S_3 precursor mixtures, with given $[\text{Sb}]/[\text{Bi}]$ ratios from 0 (Bi_2S_3) to 1 (Sb_2S_3); (b) synthesized $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ ingots; (c) CSS-deposited thin films, deposited from synthesized $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ source material at the conditions given in Table 1. Orange share corresponds to Sb, green share – to Bi, and violet share – to S.

screened in a wide range, from 400 °C to 550 °C and from 250 °C to 430 °C, for T_{so} and T_{sub} , respectively. This temperature range was chosen based on the thermodynamic considerations discussed above, as well as the previously optimized CSS processing conditions for developing Sb_2S_3 [46] and Bi_2S_3 [6]. For the deposition of each $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ system (where $0.1 \leq x \leq 0.9$), the CSS deposition time was calibrated to ensure a reasonable congruent deposition rate while maintaining a consistent film thickness of $\sim 1 \mu\text{m}$. Such absorber thickness has been tested and shown to be optimal for a range of similar absorber materials (including Sb_2S_3 , Sb_2Se_3 , SnS , and Bi_2S_3) in thin-film solar cells fabricated via CSS [6,46–49]. For the Sb-rich compositions ($(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$, $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$, Sb_2S_3), a seed layer of the same material was deposited by CSS at the substrate temperature ~ 250 °C and optimized source temperature (450–500 °C) prior to the main deposition. This strategy is widely used for other similar systems, such as Sb_2S_3 and Sb_2Se_3 [46, 48–51], especially when deposited on highly-inert substrates, such as TiO_2 ETL.

3.4. Morphological evolution and identification of optimal growth regimes

Fig. 6 shows top-view and cross-sectional SEM images of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films deposited under the conditions given in Table 1. It is essential to mention that in the figure, the SEM images are presented for the identified optimal CSS conditions of each $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ absorber layer. As shown in Fig. 6, regardless of the calibrated absorber thickness (0.5 or 1 μm), optimized CSS conditions for each system resulted in conformal coating and a densely packed morphology. As expected, 1 μm -thick absorbers exhibit larger grains than 0.5 μm -thick ones. The grain size stays in the region of 0.5–1.5 μm for the 1 μm -thick films and 0.2–1 μm for the 0.5 μm -thick films. As an important result, moving from Bi-rich systems to Sb-rich ones (from left to right in Fig. 6) the optimal T_{sub} decreased from 420 °C to 300 °C, respectively. The lowest T_{sub} of 300–320 °C, enabling dense morphology for a thin film, was identified for $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$. For the latter one, the obtained T_{sub} value is in agreement with previous findings for Sb_2S_3 CSS deposition [46]. Overall, these results indicate that Sb-rich systems can be processed at relatively low temperatures, providing more options for substrate selection, including flexible and temperature-sensitive substrates.

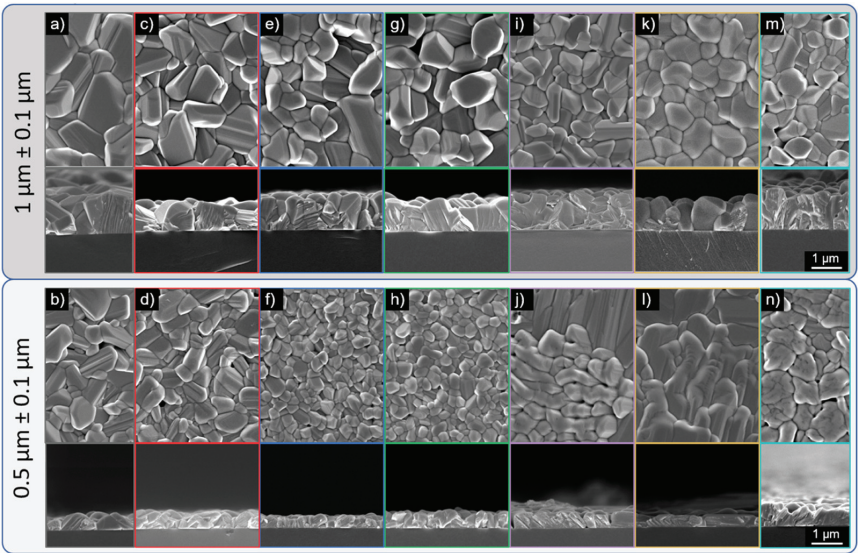


Fig. 6. Top-view and cross-sectional SEM images of (a,b) Bi_2S_3 , (c,d) $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$, (e,f) $(\text{Sb}_{0.33}\text{Bi}_{0.67})_2\text{S}_3$, (g,h) $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, (i,j) $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$, (k,l) $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$, and (m,n) Sb_2S_3 thin film absorbers deposited on soda-line glass. Optimized deposition conditions for each system are summarized in Table 1. Two sets of samples are presented – with optimized CSS deposition conditions for $1 \pm 0.1 \mu\text{m}$ and $0.5 \pm 0.1 \mu\text{m}$ thick absorbers.

Table 1
Optimized deposition conditions for the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin film absorber layers, linked to the SEM images in Fig. 6. For clarity, the conditions for the series of samples calibrated to $0.5 \mu\text{m}$ are provided. The abbreviations are defined as follows: T_{so} - source temperature, T_{sub} - substrate temperature, Log_{10} – logarithmic ratio between the supersaturation pressures above the source and substrate at given temperatures, DepRate – deposition rate.

Source material	T_{so} (°C)	T_{sub} (°C)	Log_{10} of vapor supersaturation	Deposition time (min)	DepRate (nm/min)	Need for a seed layer (Yes/No)
Bi_2S_3	460–480	410–430	0.7–1.6	40	20–50	No
$(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$	450–480	410–430	0.7–1.6	40	20–50	No
$(\text{Sb}_{0.33}\text{Bi}_{0.67})_2\text{S}_3$	460–470	380–420	0.9–2.2	30	30–70	No
$(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$	460–470	380–400	1.4–2.2	30	30–90	No
$(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$	470–480	340–360	3.3–3.6	7	50–130	Yes
$(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$	480–500	300–320	4.3–5.4	2	100–500	Yes
Sb_2S_3	490–510	280–320	4.5–6.3	1	1000–3000	Yes

For each of the investigated systems, any CSS deposition condition outside the optimal range in Table 1 resulted in a series of peculiarities in film morphology. It is obvious that for each system in Table 1, there is a large number of combinations between T_{so} , T_{sub} , and deposition time, which would result in various morphologies. However, for simplicity and clarity, here we highlight the observed effects in the morphology of $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ thin films as being very representative for Bi-rich and Sb-rich systems.

Fig. 7a. shows the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ thin film deposited at T_{sub} of 300°C (which is within the optimal T_{sub} range, see Table 1) but at lower T_{so} of 450°C for 2 min deposition (implying a low deposition rate of $\sim 100 \text{ nm/min}$). As can be seen, in this case, while the film preserves the same densely packed morphology in cross-section view, the top view shows smoother grains. For the same thin film absorber, an increase of both T_{sub} to 400°C and T_{so} to 500°C (while keeping the same deposition time of 2 min) leads to drastic changes in morphology (Fig. 7b). While the grains became more sintered, larger, and columnar in shape, a parallel effect has been observed, in which large cracks were formed throughout the whole film thickness. A similar effect was previously observed in Sb_2S_3 and explained through the difference in the thermal expansion coefficients (TECs) of orthorhombic Sb_2S_3 crystals [46]. For instance, it has been reported that the TEC of Sb_2S_3 in the [010] crystal direction is two to seven times larger than the TECs in the [100] and

[001] crystal directions [52]. This implies that, similarly to Sb_2S_3 , Sb-rich compositions could be subject to greater residual stress during the deposition process at higher temperatures. It is well-known that any accumulation of higher tensile or compressive stress will increase the probability of the formation of cracks in the films [53]. This effect can be very pronounced in Sb-rich systems, due to higher vapor pressure, and expected sublimation at lower temperatures. Therefore, higher substrate temperatures lead to crack formation in the films.

Similarly, analyzing the side effects for the $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ system, two distinct edge cases of deposition rate influence are depicted. Fig. 7c shows the thin film deposited at T_{sub} of 440°C (higher than the optimal range) and T_{so} of 480°C (within the optimal range). The deposition took 8 min, but due to the low deposition rate ($\sim 8 \text{ nm/min}$), it was not enough to fully cover the substrate, leaving multiple voids between the grains. On the opposite side, for $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ films deposited at T_{sub} of 450°C for 1 min (slightly higher than the optimal T_{sub} of 420°C) and T_{so} of 550°C (significantly higher than the optimal T_{so} of 460°C), the deposition rate was so high, that instead of the formation of a densely-packed thin film, separate needle-like and leaf-like grains, $1\text{--}10 \mu\text{m}$ in length, were formed (Fig. 7d). Such a result is consistent with previously published observations on Bi_2S_3 growth [6], which is also a typical Bi_2S_3 morphology in the case of chemically-grown thin films.

Figs. 8a and 8b summarize the CSS deposition condition diagrams for

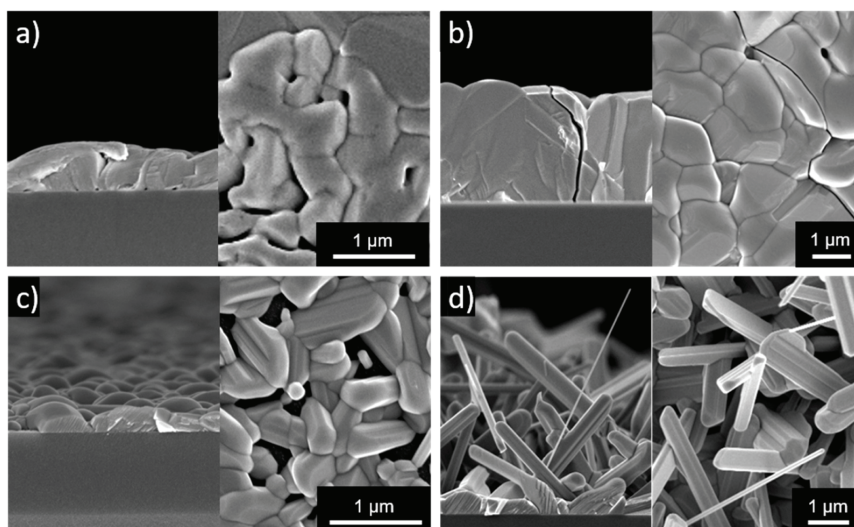


Fig. 7. Top-view and cross-sectional SEM images of absorber films deposited on glass substrate for: (a) $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ thin film, deposited with the optimized T_{sub} of 300 °C and lower-than-optimal T_{so} of 450 °C, (b) $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ thin film, deposited at higher-than-optimal T_{sub} of 400 °C and optimal T_{so} of 500 °C, (c) $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$, thin film, deposited at higher-than-optimal T_{sub} of 440 °C and optimal T_{so} of 480 °C, as well as (d) $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ thin film deposited with the higher-than-optimal T_{sub} of 450 °C and higher-than-optimal T_{so} of 550 °C.

Bi_2S_3 and Sb_2S_3 thin films, plotted as substrate temperature (T_{sub}) versus source temperature (T_{so}). These diagrams are based on our previously reported optimization studies of CSS-grown Bi_2S_3 and Sb_2S_3 thin films, and are further refined in the present work through additional parameter screening and integration into a unified growth-regime framework. Based on the systematic screening of deposition parameters described above, the investigated temperature regimes can be divided into four characteristic growth regions, reflecting different regimes governed by vapor flux, supersaturation, surface diffusion, and re-evaporation processes.

In CSS, material transport from source to substrate is possible only when $T_{\text{so}} > T_{\text{sub}}$, which confines deposition to the region below the diagonal line in Fig. 8; increasing T_{so} and the temperature difference $\Delta T = T_{\text{so}} - T_{\text{sub}}$ enhances vapor flux and supersaturation at the substrate surface. These general aspects, together with the thermodynamic considerations discussed in the first section, provide a consistent framework for interpreting the experimentally observed film morphologies. We first define the optimal growth regime (OGR), which corresponds to the deposition conditions yielding dense, homogeneous thin films and serves as a reference for interpreting the remaining growth regimes (Regimes I–III). For Bi_2S_3 (Fig. 8a), the OGR is relatively narrow and located at $T_{\text{sub}} \approx 400\text{--}430$ °C and $T_{\text{so}} \approx 420\text{--}480$ °C for glass substrates. Notably, this optimal regime can be slightly extended toward higher T_{so} values (up to a maximum of ~ 550 °C) when Bi_2S_3 is deposited on chemically and morphologically compatible substrates such as CdS or TiO_2 , as previously demonstrated in Ref. [6]. In this regime, vapor flux, supersaturation, and surface diffusion are well balanced, enabling sufficient adatom mobility and lateral grain growth, which results in compact, densely packed films with uniform morphology.

For Sb_2S_3 (Fig. 8b), the OGR is found at $T_{\text{so}} \approx 400\text{--}510$ °C and $T_{\text{sub}} \approx 280\text{--}320$ °C, exhibiting a broader tolerance toward lower substrate temperatures compared to Bi_2S_3 , in agreement with the higher volatility of Sb-containing species predicted by thermodynamic calculations (Fig. 4).

Outside the OGR window, distinct sub-optimal regimes are observed. Regime I corresponds to low source temperatures, where the vapor pressure of Bi_2S_3 or Sb_2S_3 is insufficient to sustain effective material

transport. In this kinetically limited regime, deposition rates are extremely low, and continuous films cannot be formed. Regime II occurs at substrate temperatures below the optimal range, where high supersaturation combined with limited surface diffusion favors kinetically driven, anisotropic growth. For both Bi_2S_3 and Sb_2S_3 , this results in the formation of needle-like or columnar structures, with feature size and density increasing with ΔT , indicating growth dominated by rapid nucleation rather than lateral grain coalescence. Regime III is observed at substrate temperatures above the OGR window, where re-evaporation of the deposited material becomes significant. Although vapor flux remains sufficient, enhanced re-evaporation at elevated substrate temperatures limits the effective surface diffusion time of adsorbed species, leading to non-homogeneous films, morphological distortion, and, in the case of Sb_2S_3 and Sb-rich alloys, an increased tendency toward film cracking.

The relevance of these growth regimes is illustrated by extending the same framework to $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films (Fig. 8c–d, Table 1). A direct comparison reveals that the optimized deposition windows for different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems are not symmetrically distributed between those of the individual compounds but are instead systematically shifted toward the Bi_2S_3 OGR, even at relatively high Sb contents. This behavior is consistent with the thermodynamic analysis in the first section, which indicates that Bi-rich systems are governed predominantly by BiS/ S_2 -based evaporation pathways requiring lower supersaturation, while Sb-rich systems rely increasingly on congruent Sb_2S_3 evaporation and thus demand higher supersaturation values.

This trend is further reflected in the morphology of the optimized films shown in Fig. 8, where dense, conformal coatings are achieved across the entire compositional range, while the optimal T_{sub} decreases monotonically from ~ 420 °C for Bi_2S_3 to ~ 300 °C for Sb-rich systems. Importantly, these optimized CSS conditions yield densely packed, columnar-grained absorber layers with thicknesses of 0.5–1 μm, providing a consistent morphological basis for the comparative analysis of structural and optoelectronic properties discussed below.

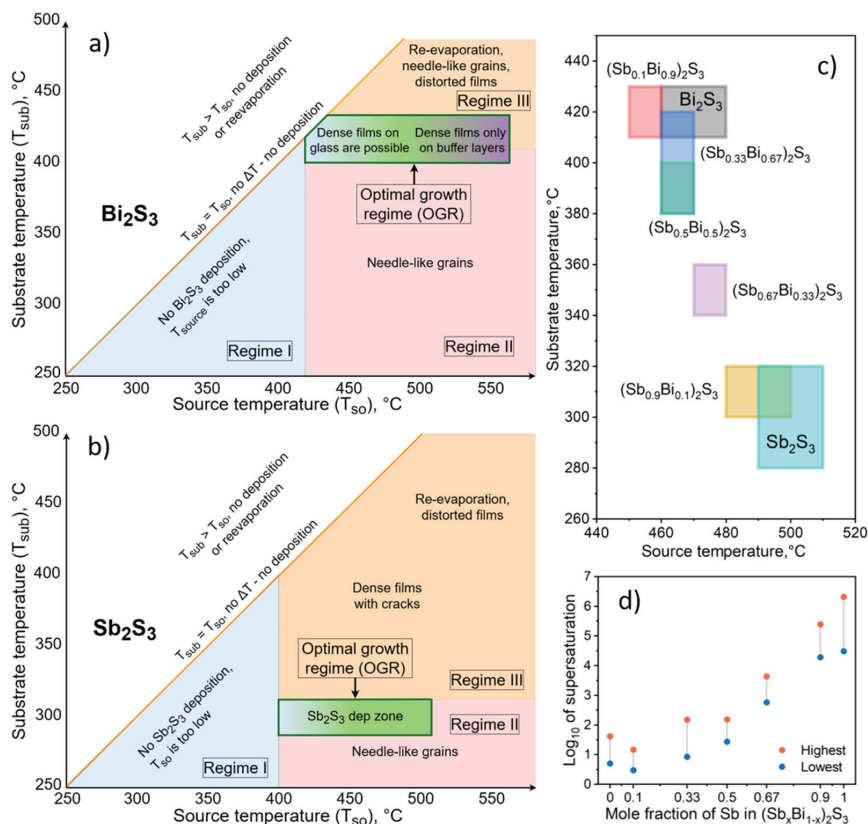


Fig. 8. (a,b) Deposition conditions (T_{sub} vs T_{so}) spaces for Bi_2S_3 and Sb_2S_3 with the optimal deposition regimes (OGR, marked in green) and three suboptimal deposition regimes (Regimes I–III); (c) the suitable temperature regions for $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems, Sb_2S_3 and Bi_2S_3 , according to Table 1; (d) $\log_{10}$ supersaturation values for the different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems.

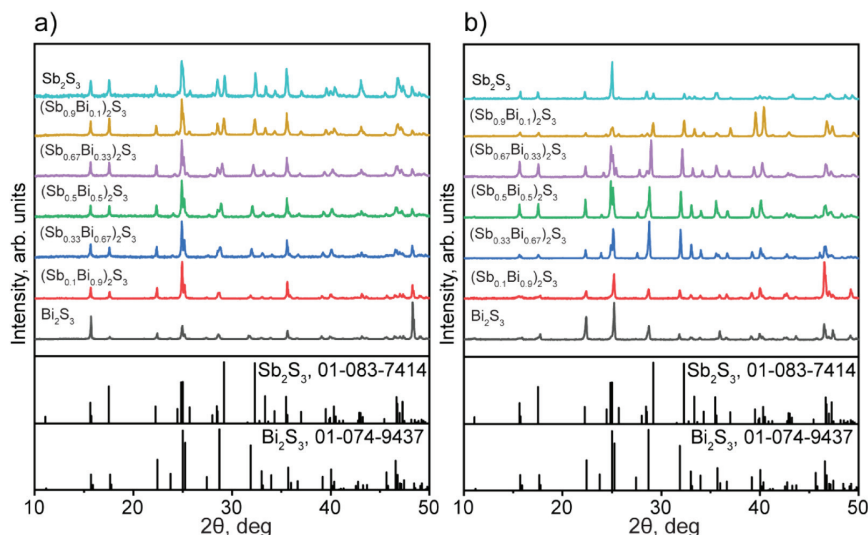


Fig. 9. XRD patterns of Bi_2S_3 , Sb_2S_3 , $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ (a) powders and (b) CSS-deposited films deposited at the conditions given in Table 1, with the reference data from ICSD cards (on the bottom).

3.5. Structural evolution and solid-solution formation

The structural properties of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems were investigated by XRD at different fabrication stages, including the synthesized source powders and the CSS-deposited thin films, and compared with reference patterns of the binary Bi_2S_3 and Sb_2S_3 . Both compounds crystallize in an orthorhombic structure (space group $Pnma$), leading to closely related diffraction patterns that enable the formation of a continuous solid-solution series.

As shown in Fig. 9, the XRD patterns of both powders and thin films exhibit the characteristic reflections of orthorhombic $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$. The main reflections at $2\theta \approx 16\text{--}18^\circ$ (201), 22° (202), and 25° (103) are present across the entire compositional range. Reflections in the 2θ regions of $28\text{--}29^\circ$ and $32\text{--}33^\circ$, corresponding to the (112) and (212) planes, are located at slightly lower angles for Bi_2S_3 compared to Sb_2S_3 . In the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems, these reflections are positioned between those of the two binary systems and shift nearly linearly with the $[\text{Sb}]/[\text{Bi}]$ ratio. Such a systematic peak shift provides reasonable evidence for the formation of a predominant single-phase solid solution across the investigated compositional range ($0.1 \leq x \leq 0.9$). In most cases, a single dominant diffraction peak is observed for each reflection, indicating good phase homogeneity. However, the appearance of weak shoulders in some reflections suggests the possible presence of local compositional fluctuations or minor secondary phases with compositions deviating slightly from the nominal stoichiometry, particularly in the mid-composition range.

For all the thin films deposited at the OGR conditions, it was found that the crystallite size (extracted from XRD patterns using Debye-Scherrer equation) varied in a very low margin, between 70 and 100 nm. Such values are characteristic for absorbers deposited by CSS with thin film thickness $0.5\text{--}1.0\ \mu\text{m}$ (Fig. 6). Such a correlation between crystallite size, grain size, and film thickness was systematically observed for similar systems, like CdTe, Sb_2S_3 , Sb_2Se_3 , SnS, etc. [46,47,54], and for absorber thickness between 1 and $2\ \mu\text{m}$, the crystallite size reaches values of $160\text{--}180\ \text{nm}$. The evolution of lattice parameters extracted from the XRD data is summarized in Fig. 10 for both powders and thin films. The lattice parameters a and c exhibit relatively small variations with composition, changing from approximately $11.24\text{--}11.33\ \text{\AA}$ and from 11.12 to $11.23\ \text{\AA}$, respectively. In contrast, lattice parameter b shows a pronounced monotonic decrease from $3.98\ \text{\AA}$ for Bi_2S_3 to $3.83\ \text{\AA}$ for Sb_2S_3 , corresponding to a contraction of approximately 4%. This anisotropic lattice evolution is consistent with the substitution of Bi^{3+} by the smaller Sb^{3+} cation and reflects the quasi-one-dimensional ribbon-like crystal structure of these compounds.

A systematic difference between powders and thin films is observed for lattice parameters a and c , which are generally larger in powders than in thin films. This behavior is commonly reported for polycrystalline thin films and can be attributed to residual stress and constrained grain growth during CSS deposition [55,56]. In contrast, lattice parameter b shows negligible differences between powders and films, suggesting that the lattice contraction along this direction is

predominantly governed by compositional effects rather than by processing-induced strain. The obtained lattice parameters are in good agreement with previously reported values for physically-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ crystals [57], as well as for the chemically-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin-films [58,59]. However, for the physically-deposited thin films, no similar data has yet been reported.

To further confirm phase formation and assess local structural homogeneity, Raman scattering spectroscopy was performed on the CSS-deposited thin films (Fig. 11). The Raman spectra of the binary Bi_2S_3 and Sb_2S_3 systems exhibit their characteristic vibrational modes, with no detectable signatures of secondary phases and relatively narrow full width at half maximum (FWHM), indicating good crystalline quality. For the solid solutions, a gradual blueshift and systematic intensity redistribution of the main Raman modes are observed with increasing Sb content, consistent with the continuous evolution of lattice dynamics in the solid-solution system and in agreement with the XRD results.

A weak Raman feature appearing at approximately $282\ \text{cm}^{-1}$ is detected for the $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ composition and persists for all films with higher Sb content. This mode corresponds to the dominant Sb_2S_3 vibration and may indicate the presence of Sb-rich region at the film surface, coexisting with the main solid-solution phase. Additionally, an increase in FWHM is observed for compositions close to $x \approx 0.5$, indicating a reduction in crystalline order, which is a typical feature of solid solutions near equimolar composition due to enhanced configurational disorder.

Overall, the combined XRD and Raman analyses confirm the

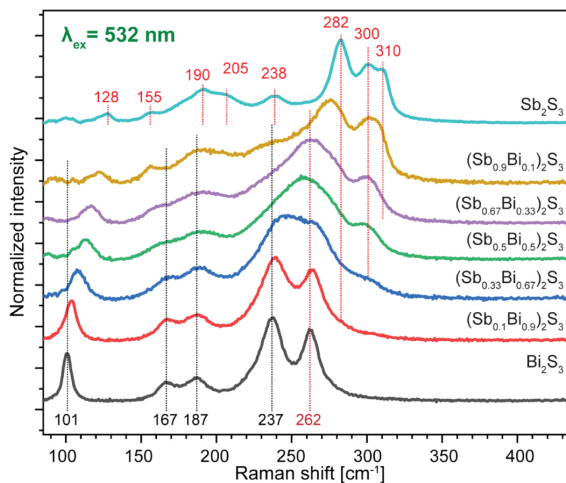


Fig. 11. Raman scattering spectra of the CSS-deposited Bi_2S_3 , Sb_2S_3 , and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films with different $[\text{Sb}]/[\text{Bi}]$ ratios.

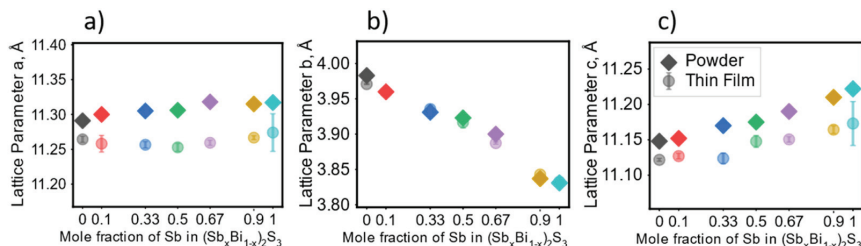


Fig. 10. (a–c) Composition-dependent differences in lattice parameters for powders (diamonds) and CSS-deposited thin films (circles) of Bi_2S_3 , Sb_2S_3 , and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions.

successful formation of orthorhombic $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions in both powder and thin-film form across the investigated compositional range. The observed systematic lattice evolution, together with the preservation of the crystal structure and good phase homogeneity under optimized CSS conditions, provides a robust structural basis for further comparative analysis of the optoelectronic properties.

3.6. Composition-dependent optoelectronic properties and charge transport

With the optimized dense-film morphology and preserved crystal structure across the entire compositional range, the optoelectronic properties of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions were systematically investigated. The electrical properties of the CSS-deposited thin films were evaluated by Hall-effect measurements, and the extracted resistivity and charge carrier density are summarized in Figs. 12a and 12b. A pronounced composition-dependent trend is observed across the solid-solution series. While Bi_2S_3 exhibits low resistivity and high electron concentration, consistent with its intrinsic n-type character, increasing Sb content leads to a strong increase in resistivity accompanied by a gradual reduction in carrier density. While the $(\text{Sb}_{0.33}\text{Bi}_{0.67})_2\text{S}_3$ is still a predominantly n-type material, starting from $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, a p-type conductivity prevails. Overall, moving from Bi-rich compositions (e.g. Bi_2S_3 and $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$) to Sb-rich compositions (e.g. $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$), the resistivity spans a wide range from approximately $5 \Omega\cdot\text{cm}$ to $10^6 \Omega\cdot\text{cm}$, and carrier concentration from $\sim 10^{17} \text{ 1/cm}^3$ to $\sim 10^{11} \text{ 1/cm}^3$. For the mobility measurements, no clear trend has been observed with values between $3 \text{ cm}^2/\text{Vs}$ and $11 \text{ cm}^2/\text{Vs}$ for the entire compositional range. Such values are pertinent (and in agreement with previously reported values in similar systems, such as SnS [47]), considering the particularity of Hall measurements in the lateral direction on glass substrates. It is expected that measurements in the vertical direction (e.g. time-of-flight and carrier dynamic measurements) will provide higher values.

Notably, the incorporation of a small amount of the secondary cation does not immediately alter the electrical behavior. Both $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ exhibit transport properties comparable to those of their respective host binary systems, indicating that in the low substitution limit of the solid solution, the dominant conduction mechanism is not significantly perturbed. This behavior suggests that, at low substitution levels within the solid-solution series, the electrical properties remain largely governed by the intrinsic defect chemistry of the host binary system, whereas increasing alloying toward intermediate and Sb-rich compositions leads to a progressive modification of the electronic structure and transport characteristics.

At the microscopic level, this behavior can be tentatively rationalized by considering the evolution of defect states upon cation substitution. Importantly, the observed transport behavior at low Bi incorporation levels is consistent with our recent detailed analysis of the electronic structure and defect states in Bi_2S_3 , Sb_2S_3 , and their solid solutions using energy-resolved electrochemical impedance

spectroscopy (ER-EIS) [60]. Therein, it was demonstrated that pristine Sb_2S_3 exhibits pronounced deep defect states within the bandgap, which act as efficient non-radiative recombination centers and are considered a major limitation for achieving high open-circuit voltages in Sb_2S_3 -based solar cells.

Notably, already a small Bi incorporation corresponding to the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ composition was shown to transform these deep defect states into shallow ones, while largely preserving the band edge positions characteristic of Sb_2S_3 . This defect “healing” effect provides a microscopic explanation for the retention of Sb_2S_3 -like transport characteristics at low alloying levels and highlights cation substitution as a potential effective strategy to suppress mid-gap defects without fundamentally altering the host electronic structure, thereby offering a promising pathway toward improved electrical performance and, ultimately, higher device voltages.

The optical properties of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution thin films were investigated by UV-Vis absorption spectroscopy to evaluate the evolution of the bandgap values as a function of composition. All films exhibit strong absorption throughout the visible spectral range, enabling reliable extraction of optical bandgaps using Tauc analysis. The absorption edges show well-defined linear regions in both direct and indirect transition representations, indicating that both transition types may contribute to the optical response of these systems. A systematic and nearly monotonic widening of the optical bandgap is observed with increasing Sb content across the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution series. The direct optical bandgap increases from $1.31 \pm 0.03 \text{ eV}$ for Bi_2S_3 to $1.72 \pm 0.16 \text{ eV}$ for Sb_2S_3 , while the indirect bandgap increases from $0.88 \pm 0.12 \text{ eV}$ to $1.57 \pm 0.18 \text{ eV}$ over the same compositional range. On the one hand, the extracted direct bandgap values are in good agreement with those previously reported for solution-processed Bi_2S_3 and Sb_2S_3 thin films, indicating that the band-edge positions are largely preserved across different deposition routes [61]. On the other hand, experimental reports on indirect bandgap energies in these materials remain scarce, as indirect transitions have so far been discussed primarily on the basis of theoretical predictions. In this context, the present absorption analysis provides experimental estimates of indirect transition energies that are consistent with theoretically predicted values [30], supporting the coexistence of direct and indirect optical transitions in this class of quasi-one-dimensional chalcogenides. Notably, for Sb_2S_3 the energy difference between the direct and indirect transitions remains relatively small ($\Delta E \approx 0.15 \text{ eV}$), in line with previous experimental and theoretical studies and suggesting the presence of multiple optically active transition pathways [30]. Importantly, the smooth evolution of the optical bandgap across the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution series confirms that cation substitution enables effective bandgap tunability without introducing abrupt changes in optical absorption behavior, even in the dilute substitution regime. This independent tunability of optical bandgap and electrical conductivity highlights the versatility of the system for absorber optimization, particularly in the context of PV applications where balancing light absorption, carrier extraction, and recombination losses is critical.

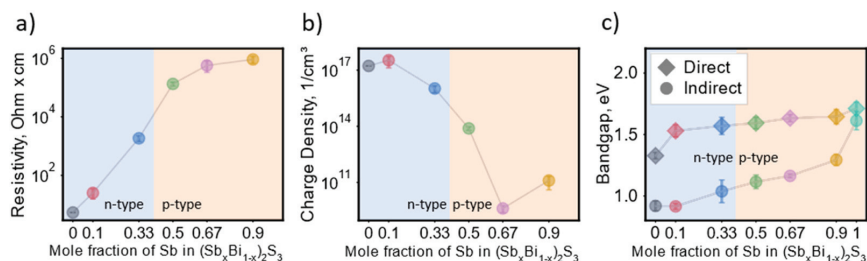


Fig. 12. Composition-dependent change of the (a) resistivity, (b) charge density measured by Hall measurement, and the (c) direct and indirect transition bandgaps in $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films measured by UV-Vis. Predominant conductivity type is highlighted by the background color, blue for n-type and orange for p-type.

3.7. Low-temperature photoluminescence and radiative recombination pathways

To gain insight into radiative recombination processes, we next performed photoluminescence (PL) measurements. To the best of our knowledge, PL studies of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions have not been reported previously, neither at room temperature nor at low temperatures. Here, low-temperature PL is employed as a first experimental probe of radiative recombination in CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, with direct comparison to reference PL spectra of the binary Bi_2S_3 and Sb_2S_3 compounds included in Fig. 13.

In our previous studies on the binary reference systems, low-temperature PL of Bi_2S_3 was characterized by broad, multi-band emissions, with the dominant band attributed to deep donor–deep acceptor (DD–DA) recombination, whereas Sb_2S_3 exhibited two distinct contributions: a narrow band-to-band emission near 1.72 eV and a broader asymmetric band around 1.40 eV, assigned to donor–acceptor pair (DAP)-type recombination [6,46]. These well-established reference behaviors provide a robust framework for comparative interpretation of the PL spectra of the solid-solution films. For the alloyed compositions, detectable PL emission was obtained only at low temperatures, with rapid thermal quenching observed upon increasing temperature. As a consequence, temperature- and excitation-power-dependent PL measurements—required for unambiguous identification of recombination channels—could not be performed. At the same time, across all the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution series, the PL spectra exhibit broad and asymmetric emission bands, with peak energies systematically below the optical bandgaps extracted from UV–Vis absorption. This may indicate that radiative recombination is not dominated by free band-to-band transitions, but instead involves localized electronic states, consistent with the behavior of quasi-one-dimensional chalcogenides [62–65]. For instance, similar low-temperature PL characteristics have been reported for $\text{Sb}_2(\text{SeS}_2)_3$ solid solutions, where asymmetric emission bands were attributed to exciton-assisted and defect-related recombination accompanied by strong electron–phonon coupling [66, 67], supporting the relevance of such possible mechanisms in the present system. At the same time, these PL observations are fully consistent with our recent ER-EIS analysis [60], which demonstrated that pristine Sb_2S_3 is dominated by deep mid-gap defect states, whereas already a small Bi incorporation corresponding to the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ composition leads to a transformation of deep defects into shallow states, while largely preserving the Sb_2S_3 -like band-edge positions. Within this context, the absence of sharp band-edge PL features in the solid

solutions, despite the suppression of deep mid-gap states, suggests that radiative recombination is probably governed primarily by shallow localized states and exciton-assisted processes, rather than by deep defect levels. At this stage, it is not clear whether the quasi-one-dimensional ribbon structure of the material has an implication for the PL features of this material. Overall, the PL results presented here constitute a first step toward understanding radiative recombination in the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution system. Establishing a direct correlation between the defect energetics revealed by ER-EIS and the dominant radiative recombination pathways will require systematic temperature- and excitation-power-dependent PL studies, which represent an important direction for future work and will be critical for linking defect physics to device-relevant performance.

3.8. Proof-of-concept solar cell demonstration

Having established that $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution thin films can be reproducibly deposited with well-controlled structural and optoelectronic properties, we next assess their functionality as absorber layers in thin-film solar cells. Rather than pursuing full device optimization across all compositions, which lies beyond the scope of this study, our aim is to demonstrate a proof-of-concept photovoltaic device validating the viability of CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ absorbers. For this purpose, $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ absorber was selected based on two considerations: (i) ER-EIS analysis showed that even limited Bi incorporation transforms deep mid-gap defects into shallow states while preserving Sb_2S_3 -like band edges [60], favourable for achieving higher open-circuit voltages; and (ii) its relatively wide bandgap (~1.6–1.7 eV) is well suited for wide-bandgap absorber applications, including tandem top cells and indoor PV.

Based on the previously identified optimal growth regime (OGR), superstrate devices with the architecture glass/FTO/CdS/ $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3/\text{Au}$ were fabricated without further optimization of the CSS deposition parameters. CdS was selected as an ETL due to its maturity in development and compatibility with a wide range of chalcogenide device platforms [6,46,47,68,69]. The absorber was deposited at $T_{\text{sub}} \sim 300^\circ\text{C}$ and $T_{\text{so}} \sim 500^\circ\text{C}$ for ~2 min, yielding compact films with thicknesses of ~0.8 μm . The CdS ETL was deposited under established conditions previously optimized for Bi_2S_3 - and Sb_2S_3 -based devices [6,46]. A cross-sectional SEM image and schematic of the device structure are shown in Fig. 14a–b, confirming the formation of a continuous multilayer stack. The PV performance of the proof-of-concept devices is summarized in Fig. 14c–h.

The representative current–voltage (J–V) curve (Fig. 14c) yields an open-circuit voltage (V_{OC}) of 581 mV, a short-circuit current density (J_{SC}) of 6.62 mA cm^{-2} , a fill factor (FF) of 35.6%, and a power-conversion efficiency (PCE) of 1.37%. Statistical distributions of the device parameters extracted from multiple cells are shown in Fig. 14e–h, demonstrating reasonable reproducibility despite the absence of dedicated device optimization. Compared to our previously reported Bi_2S_3 -based solar cells, the present $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ device exhibits a marked improvement across all photovoltaic parameters, most notably a nearly three-fold increase in V_{OC} , which can be attributed to the larger bandgap and probably to the modified defect landscape induced by Bi incorporation. At the same time, the achieved V_{OC} values are already comparable to those reported for CSS-processed Sb_2S_3 devices (Table 2) [46], highlighting the promise of Bi-alloyed absorbers even at this early proof-of-concept stage. The preliminary assessment of the device stability (kept in a plastic box under dark and air exposure, without encapsulation) shows that the cell retains the PCE values of 1.33% after 1 month, 1.26% after 3 months, and 1.17% after 6 months. This suggests a potential for high stability of the device for long-term operation.

At the same time, the contribution of the electrical parameters (Fig. 12) on the performance of the device should not be excluded. As shown in Fig. 12a,b, $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ films exhibit high resistivity (~ $10^6 \Omega\text{-cm}$) and low carrier density of ~ 10^{11} cm^{-3} . This is in line with the

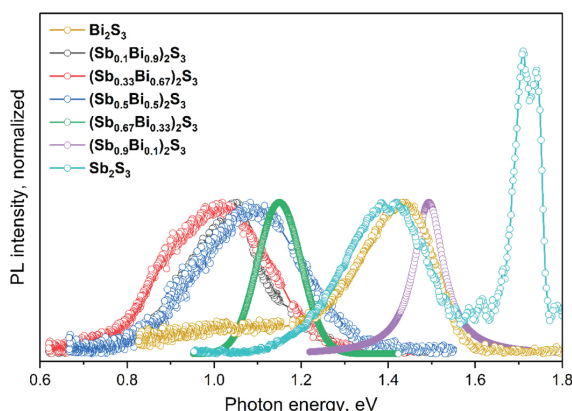


Fig. 13. Low-temperature photoluminescence spectra for Sb_2S_3 , Bi_2S_3 , and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films, measured at the wavelength of 266 nm, the maximum average power of 8 mW, and a temperature of 4 K.

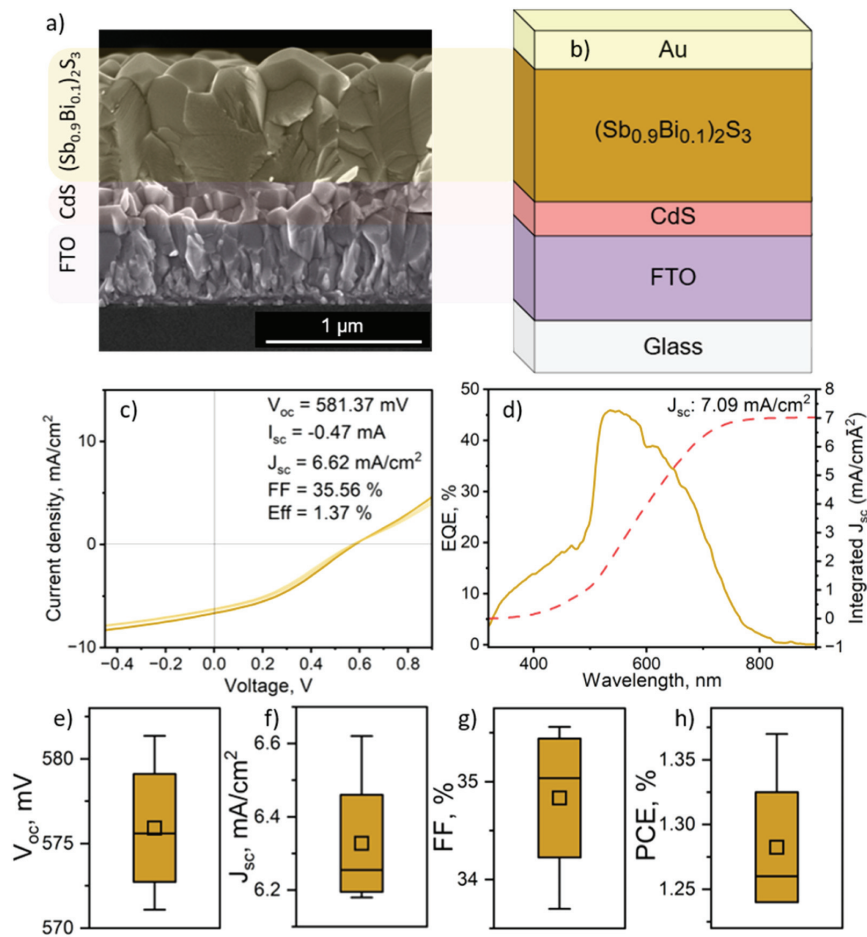


Fig. 14. The $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ devices with the architecture of glass/FTO/CdS/ $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ /Au, featured on the (a) SEM cross-section image and (b) a schematic depiction, with the main photovoltaic characteristics including (c) J-V curves, (d) EQE response, (e) open circuit voltage (V_{oc}), (f) short circuit current density (J_{sc}), (g) fill factor (FF), and (h) photoconversion efficiency (PCE).

Table 2
Reported PCEs and PV parameters for Sb_2S_3 and Bi_2S_3 -based devices with absorbers deposited by CSS.

Absorber material	Reported device architecture	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Ref.
Sb_2S_3	glass/FTO/CdS/ Sb_2S_3 /Au	700	9	45.3	2.86	[70]
Sb_2S_3	glass/FTO/CdS/ Sb_2S_3 /Au	680	11.5	48	3.80	[46]
Sb_2S_3	glass/FTO/CdS/ Sb_2S_3 /Au	743	14.12	45.6	4.78	[71]
Sb_2S_3	glass/FTO/CdS/ Sb_2S_3 /Spiro-OMeTAD/Au	739	15.65	51.8	5.81	[72]
Bi_2S_3	glass/FTO/CdS/ Bi_2S_3 /Au	90	3.5	23	0.10	[6]
$(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$	glass/FTO/CdS/ $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ /Au	581	6.6	35.5	1.37	This work

high series resistance value of 5–8 $\text{Ohm}\cdot\text{cm}^2$, obtained for the device, implying contribution from both bulk resistance effects and non-optimal

interfaces (as suggested above - presence of a rollover anomaly). On one hand, the low carrier concentration implies that the space charge region (SCR) is virtually located within the absorber, which is known to be suitable for the p-n heterojunction model [73]. On the other hand, the high resistivity (and, probably, presence of other deep defects in the absorber [60]) may limit the carrier lifetime and diffusion length, and, hence, the carrier collection in the device. Contributions from back-contact-related barriers cannot be excluded at this stage. These observations indicate that the current device performance is limited by both interface quality and deficient carrier transport due to the highly resistive absorber in a p-n heterojunction device.

Overall, this proof-of-concept study validates the PV functionality of CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution absorbers, even in the absence of device-level optimization. The encouraging performance of the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ device, together with the demonstrated bandgap, carrier density, and defect-state tunability across the solid-solution series, provides strong confidence that significantly higher efficiencies can be achieved through systematic interface engineering, absorber thickness optimization, and exploration of alternative device architectures such as n-i-p configurations [74]. So far, our results on a proof-of-concept device show promising potential; however, there is significant room for

further improvement of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, including testing and validation with alternative ETLs (e.g., TiO_2 , ZnO , SnO_2) [75–79]. Beyond conventional thin-film photovoltaics, these results open opportunities for tandem, indoor PV, and other optoelectronic applications where tailored bandgap and defect control are essential.

4. Conclusions

This work establishes, for the first time, a composition-tunable $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution thin-film platform developed by close-spaced sublimation, linking composition, vapor-phase equilibrium calculations, growth regimes, thin-film properties, and proof of concept PV device functionality within a single framework. Through solid-solution ingot synthesis combined with thermodynamically guided CSS screening, composition-dependent growth regimes were identified that enable the reproducible formation of dense, homogeneous absorber layers across the entire $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution compositional range. Optimal CSS growth regimes were established within $T_{\text{sub}} \approx 280\text{--}430^\circ\text{C}$ and $T_{\text{so}} \approx 400\text{--}550^\circ\text{C}$, yielding compact films with thicknesses of $\sim 0.5\text{--}1\ \mu\text{m}$. Structural characterization confirms the formation of single-phase orthorhombic solid solutions with continuous lattice evolution and no macroscopic phase separation. Optical and electrical characterization demonstrates broad and continuous tunability of optoelectronic properties, with the bandgap evolution from $\sim 1.3\text{ eV}$ to $\sim 1.7\text{ eV}$ and carrier densities varying over more than two orders of magnitude across the solid-solution series. Experimental estimates of indirect transition energies are consistent with theoretical predictions, supporting the coexistence of direct and indirect optical transitions. Low-temperature photoluminescence measurements, reported here for the first time for CSS-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ films, suggest radiative recombination involving localized and exciton-assisted processes.

Finally, a proof-of-concept solar cell based on a $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ absorber, fabricated without device-level optimization, demonstrates the PV viability of CSS-deposited solid-solution absorbers, achieving a PCE of $\sim 1.4\%$. Overall, these results show that alloying within the $\text{Bi}_2\text{S}_3\text{--Sb}_2\text{S}_3$ system provides a robust route to tune growth behavior and optoelectronic properties in quasi-one-dimensional chalcogenide absorbers, offering a strong foundation for future optimization toward tandem photovoltaics, indoor energy harvesting, and related optoelectronic applications.

CRedit authorship contribution statement

Gleb Colibaba: Writing – review & editing, Methodology, Formal analysis. **Evelina Dudutienė:** Writing – review & editing, Investigation. **Daria Milišević:** Writing – review & editing, Formal analysis. **Ilona Oja Acik:** Writing – review & editing. **Malle Krunk:** Writing – review & editing. **Mykhailo A. Koltsov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Data curation, Conceptualization. **Nicolae Spalatu:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Data curation, Conceptualization. **Victoria Rotaru:** Investigation. **Maxim Guc:** Writing – review & editing, Investigation. **Jaan Hiie:** Writing – review & editing. **Dumitru Untila:** Writing – review & editing.

Declaration of Competing Interest

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Appendix 3

Publication III

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Understanding the correlation between deposition conditions and nanoribbon orientation in close-spaced sublimated $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin film solid solutions

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ABSTRACT

Quasi-one-dimensional (Q1D) chalcogenide semiconductors are emerging thin-film absorber candidates whose photovoltaic performance is strongly connected to the nanoribbon orientation. Among them, $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions provide composition-tunable optoelectronic properties, but the interrelation between close-spaced sublimation (CSS) growth conditions and nanoribbon orientation has not been systematically established. Here, we combine Bragg-Brentano XRD with texture coefficients (TC) and ribbon carrier transport (RCT) quantification, texture-XRD pole figure analysis, and electron backscatter diffraction (EBSD) method to assess nanoribbon orientation across $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films ($x = 0, 0.1, 0.33, 0.5, 0.67, 0.9$) deposited on soda-lime glass. For each composition, nanoribbon orientation is characterized against deposition rate and source/substrate temperature; within the tested deposition conditions window, the most favourable texture is achieved for $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ grown at $T_{\text{so}} = 460^\circ\text{C}$ and $T_{\text{sub}} = 380^\circ\text{C}$, with $\text{RCT} = 82.3\%$ and a nanoribbon tilt angle $\alpha' \approx 35^\circ$ from the substrate normal; Bi_2S_3 and Sb_2S_3 favour more lateral orientations. The three independent texture characterization methods agree on α' to within 9° , validating the protocol. GIXRD depth profiling reveals that all lattice parameters and microstrain increase from the substrate interface toward the film surface. Non-textured films exhibit the most prominent aggregation of microstrain. These findings establish quantitative texture versus process correlations for $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ and provide guidance for absorber optimisation on technologically relevant substrates such as CdS and TiO_2 .

1. Introduction

Solar cell technologies based on chalcogenide photovoltaic (PV) materials, such as cadmium telluride and copper indium gallium selenide (CIGS), have been successfully competing in power conversion efficiency (PCE) with silicon-based solar cells, with the highest reported PCE of around 23% [1–3]. However, their implementation may be limited because of the scarcity and high price of tellurium, indium, and gallium. Therefore, the search for new semiconductor materials is among the key tasks for the thin-film PV field.

In recent decades, multiple emerging inorganic chalcogenide materials have become the focus of active research as PV absorbers, such as the $(\text{Sb,Bi})_2(\text{S,Se})_3$ family – comprising the four binary systems Sb_2S_3 , Sb_2Se_3 , Bi_2S_3 , and Bi_2Se_3 together with their ternary and quaternary

alloys and solid solutions. These chalcogenide compounds (except for Bi_2Se_3) with orthorhombic structure are composed of abundant elements, possess suitable band gaps (0.9–1.8 eV), and exhibit low toxicity. Orthorhombic $(\text{Sb,Bi})_2(\text{S,Se})_3$ materials share a quasi-one-dimensional (Q1D) structure with the $[(\text{Sb,Bi})_4(\text{S,Se})_6]_n$ atomic chains (nanoribbons) held together through weak van der Waals forces [4,5]. Since vertical nanoribbon alignment in Q1D absorbers is expected to provide an improved charge transport pathway [6,7], the orientation of nanoribbons in thin films is a critical factor governing the PV performance of these materials.

Identifying and optimizing earth-abundant chalcogenide absorbers has led to extensive research into the $(\text{Sb,Bi})_2(\text{S,Se})_3$ systems (Fig. 1, Table 1). Sb_2Se_3 is the most researched binary member of this family of materials, with the highest achieved PCE of 10.57% [8], followed by

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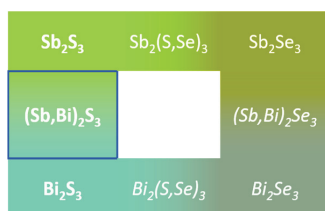


Fig. 1. (Sb,Bi)₂(S,Se)₃ materials with the highlighted (Sb,Bi)₂Se₃ as a solid solution of interest. Materials with non-orthorhombic phases (based on Bi₂Se₃) are given in *italic*.

Sb_2S_3 with a PCE of 8% [17]. Both of the antimony chalcogenides are primarily p-type semiconductors. Bi_2S_3 -based solar cells achieved 3.3% PCE [14] for an absorber in the form of randomly-oriented nanowires and about 0.75% PCE [18] for an absorber in the form of a densely-packed thin film. Bi_2Se_3 crystallizes in a rhombohedral space group ($R\bar{3}mH$ or $R\bar{3}mR$) with a band gap of 0.35 eV [16]. The highest PCE for a solar cell is 0.28% [19]. Both of the bismuth chalcogenides tend to be n-type semiconductors. Due to their structural similarity [20], alloying of the binary $(Sb, Bi)_2(S, Se)_3$ compounds to achieve more optimal structural and optoelectronic properties was a tempting research direction. Unlike Bi_2Se_3 -based materials, which may undergo the transition between rhombohedral and orthorhombic structures depending on their composition [21,22], both $Sb_2(S, Se)_3$ and $(Sb, Bi)_2S_3$

Table 1

Main properties of the binary systems (Sb_2S_3 , Sb_2Se_3 , Bi_2S_3 , Bi_2Se_3) of the $(\text{Sb,Bi})_2(\text{S,Se})_3$ family as the thin-film PV absorbers. Lattice parameters for orthorhombic materials are given according to the Pnma space group symmetry.

	Structure	a, b, c lattice parameters, Å	Band gap, eV	Prevailing conductivity type	Resistivity, Ohm*cm	Highest PCE, %
Sb_2Se_3 [8–10]	orthorhombic $Pnma$	11.79, 3.98, 11.67	1.1–1.3	P	10^{15}	10.57%
Sb_2S_3 [11–13]	orthorhombic $Pnma$	11.23, 3.75, 11.31	1.7–1.8	P	10^6	8%
Bi_2S_3 [14,15]	orthorhombic, $Pnma$	11.26, 3.95, 11.12	0.9–1.1 (indirect) 1.3–1.4 (direct)	N	10	3.3%
Bi_2Se_3 [16]	rhombohedral, $R\bar{3}mH$ or $R\bar{3}mR$	4.14, 4.14, 28.66, $\gamma = 120^\circ$	0.35	N	10^{-5}	0.28%

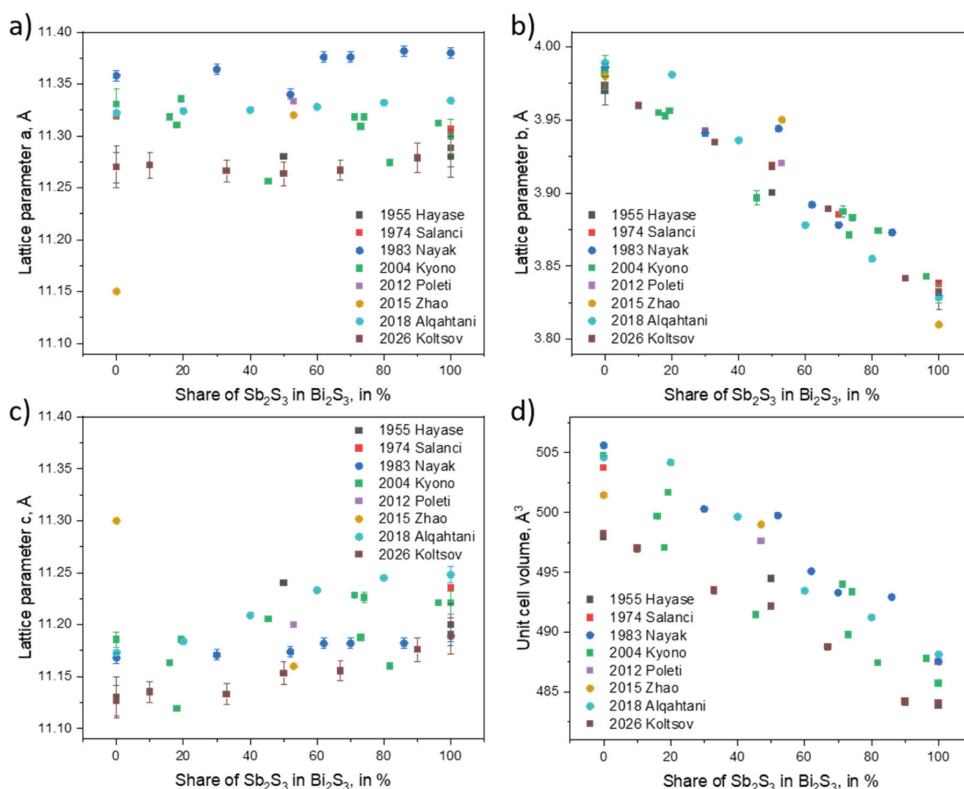


Fig. 2. Lattice parameters and unit cell volume of the (Sb,Bi)₂S₃ solid solutions according to the literature [24,26,30,37,38,40–42]. Physical synthesis is marked with squares, chemical synthesis with circles.

are orthorhombic independently of the ratio between the anions and cations, respectively. Compared with Sb_2S_3 and Sb_2Se_3 , $Sb_2(S,Se)_3$ is the most thoroughly researched PV material. It was reported to have a higher PCE than both Sb_2S_3 and Sb_2Se_3 , with the current highest efficiency of 10.8% [23]. $Sb_2(S,Se)_3$ is the most well-researched solid solution among the $(Sb,Bi)_2(S,Se)_3$ materials, with 38 studies about it published in 2022 alone [9].

Compared with $Sb_2(S,Se)_3$, the $(Sb,Bi)_2S_3$ solid solution has received considerably less attention. Unlike $Sb_2(S,Se)_3$, which combines two p-type materials, $(Sb,Bi)_2S_3$ is a solid solution of p-type Sb_2S_3 and n-type Bi_2S_3 , providing an opportunity for a broader range of applications [24]. The phenomenon of full intersolubility between Bi_2S_3 and Sb_2S_3 was first described in 1919 [25], and the early mineralogical research was advanced by the discovery of $(Sb,Bi)_2S_3$ as a component of Au-Ag-Cu ores in the mine of Horobetsu, Japan [26,27], where thermogravimetric properties of different [Sb]/[Bi] ratios were characterized [28,29], clarifying the melting points of the solid solutions.

Most of the studies regarding $(Sb,Bi)_2S_3$ films focus on chemical deposition methods, such as the dip-dry method [30,31], spin-coating deposition [32], cation exchange [33,34], and hydrothermal deposition [35,36]. However, there has been little research on the physical methods of $(Sb,Bi)_2S_3$ alloying or deposition of $(Sb,Bi)_2S_3$ thin films [37–39]. In a previous study [24], we developed the technology of preparing $(Sb,Bi)_2S_3$ solid solutions and depositing homogeneous, densely-packed $(Sb,Bi)_2S_3$ thin films with different [Sb]/[Bi] ratios via close-spaced sublimation (CSS), characterizing their chemical, structural, morphological, and optoelectronic properties.

From a structural point of view, there are clear complications in characterizing the crystal structure of the $(Sb,Bi)_2S_3$ solid solutions. Both Sb_2S_3 and Bi_2S_3 are orthorhombic with very similar lattice parameters, leading to nearly identical diffraction patterns [24] and overlapping of the most prominent reflections. This makes it difficult to define the nanoribbon orientation of a polycrystalline film using the texture coefficient (TC) and related approaches, creating a need for more in-depth investigation by texture-XRD, specifically, pole figure analysis. In most of the studies on this topic, the only available structural information was the XRD pattern, with, in some cases, lattice parameter values. A shift of the main reflections [30] and a decrease in lattice parameters [40] were briefly mentioned. The literature data regarding the lattice parameters a , b , and c of the $(Sb,Bi)_2S_3$ solid solutions are summarized in Fig. 2; notably, the values reported in [41] represent a significant outlier, while the remaining data show that lattice parameters a , b , and, consequently, the unit cell volumes, were generally larger for the chemically-synthesized thin films than for the physically-synthesized crystals and thin films.

At the same time, controlled doping and defect regulation in Q1D chalcogenide absorbers are hindered by the anisotropic crystal structure and the point-defect chemistry specific to these materials, which limits the achievable open-circuit voltage [43]. In the $(Sb_xBi_{1-x})_2S_3$ system, our companion study [44] showed by energy-resolved electrochemical impedance spectroscopy that already at modest Bi incorporation, the deep mid-gap defect states of Sb_2S_3 shift to shallow positions. The present work focuses on a complementary aspect: controlling nanoribbon orientation (texture) to optimize the charge transport paths in the absorber.

However, no consistent information on the changes in texture of $(Sb,Bi)_2S_3$ thin films depending on their chemical composition or deposition conditions has been published (independent of the employed deposition technique), which represents a knowledge gap to be filled. Due to the scarcity of research on physically deposited films, their crystal growth as a process remains underresearched. Furthermore, no studies employing structural depth profiling of $(Sb,Bi)_2S_3$ by means of grazing incidence XRD (GIXRD) have been reported, which may be indicated as a second knowledge gap. The present work aims to address both of these gaps through a systematic, multi-technique structural investigation of CSS-deposited $(Sb_xBi_{1-x})_2S_3$ thin films ($x = 0, 0.1, 0.33, 0.5, 0.67, 0.9$),

combining BBXRD-based texture quantification, pole figure analysis, EBSD, and GIXRD depth profiling, in order to determine the deposition conditions that yield optimal nanoribbon orientation for PV applications. These findings are intended to establish the process-texture correlations needed for the subsequent development of $(Sb_xBi_{1-x})_2S_3$ absorber layers on relevant electron transport layers (ETLs), such as CdS and TiO_2 .

2. Experimental

2.1. $(Sb_xBi_{1-x})_2S_3$ solid solution preparation and thin film deposition

Solid solution synthesis and CSS thin-film deposition procedures, including the deposition conditions (source temperature T_{so} , substrate temperature T_{sub} , deposition time), are thoroughly described in a previous study [24]. $(Sb_xBi_{1-x})_2S_3$ solid solutions were manufactured from Sb_2S_3 and Bi_2S_3 binary materials sourced from ThermoElectric with 5 N purity. The lump was ground with a mortar and pestle and mixed, with molar shares of 10.0%, 33.3%, 50.0%, 66.7%, and 90.0% Sb_2S_3 in Bi_2S_3 , respectively. The resulting mixes were vacuumized in quartz ampoules and heated to 800 °C for 1 h to produce $(Sb_xBi_{1-x})_2S_3$ (where $x = 0, 0.1, 0.33, 0.5, 0.67$, and 0.9) solid solutions. After cooling, the resulting ingots were crushed into powder to prepare a source material for CSS thin-film deposition. 2.3 mm thick soda-lime glass from Sigma Aldrich was used as a substrate for the deposition of $(Sb_xBi_{1-x})_2S_3$ solid solution thin films.

2.2. $(Sb_xBi_{1-x})_2S_3$ powder and thin film characterization

XRF characterization was conducted on a Bruker M4 Tornado spectrometer. Bragg-Brentano XRD (BBXRD) patterns were obtained using a Rigaku Ultima IV diffractometer and a Bruker D8 diffractometer, respectively, with Cu $K\alpha$ radiation ($\lambda = 1.54$ Å, 40 kV, 40 mA). Grazing incidence XRD (GIXRD) measurements were performed using a PANalytical X'pert Pro MPD diffractometer with Cu- $K\alpha_1$ -radiation ($\lambda = 1.54$ Å). To obtain depth profile information, the grazing angle was set at 0.5°, 2.5°, and 5° for Bi_2S_3 and solid solutions up to $(Sb_{0.5}Bi_{0.5})_2S_3$ and at 0.5°, 1.5°, and 3° for the $(Sb_{0.67}Bi_{0.33})_2S_3$ and $(Sb_{0.9}Bi_{0.1})_2S_3$ solid solutions, to get the structure information about the regions shallower than 65–85 nm, 240–370 nm, and 475–750 nm (Supplementary material, Figure S2), respectively, similarly to the procedure in [45]. Le Bail analysis [46] was conducted for both BBXRD and GIXRD data to obtain the lattice parameters and, in the case of GIXRD, microstrain values, using FullProf software [47,48]. Texture-XRD analysis was conducted using a PANalytical X'Pert Pro MRD X-ray diffractometer equipped with an Eulerian cradle employing two-axis scans along ϕ and χ in increments of 5° each. The intensity distribution was recorded along full circles (from 0° to 360°) and at different sample tilts (from 0° to 85°). Electron backscatter diffraction (EBSD) orientation mapping was done using a Zeiss UltraPlus scanning electron microscope equipped with an Oxford Instruments Symmetry EBSD detector. The measurements were conducted at a beam energy of 20 keV and a beam current of about 6 nA, using the acquisition and evaluation software AZtec.

3. Results and discussion

In a previous study [24], deposition-regime maps for CSS-grown $(Sb_xBi_{1-x})_2S_3$ thin film absorbers were established, identifying the substrate/source temperature combinations required for obtaining dense, continuous, and morphologically suitable films across the composition range. Building upon this framework, the present study focuses specifically on texture evolution within these morphology-compatible growth windows. Accordingly, the objective of the current work was not to maximize RCT values alone, but rather to identify deposition conditions simultaneously providing both suitable absorber morphology and favourable nanoribbon orientation for potential PV applications. For

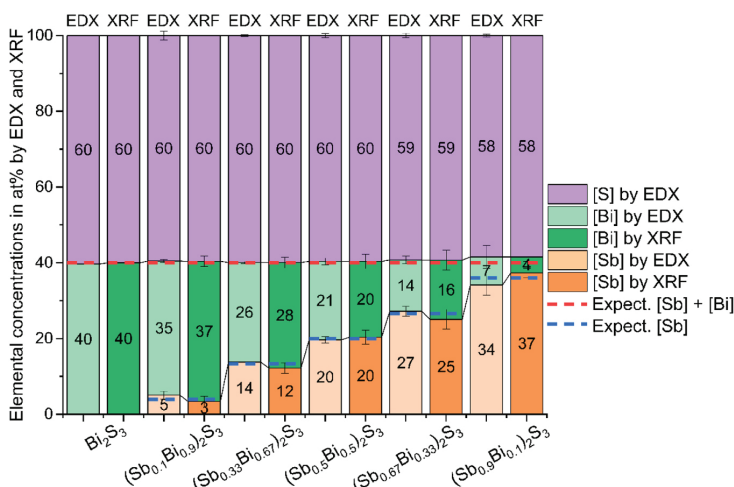


Fig. 3. Chemical composition of the Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films according to (a) XRF and (b) EDX characterization.

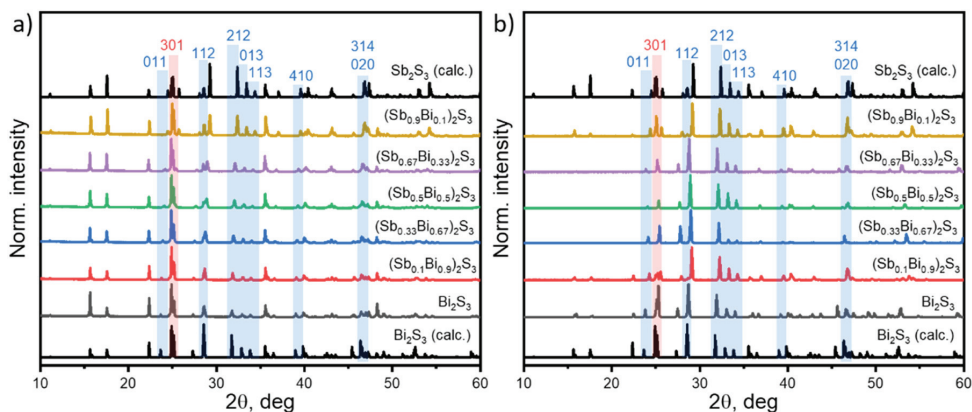


Fig. 4. BBXRD patterns of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ powders (a) and thin films (b) with different [Sb]/[Bi] ratios deposited on plain soda-lime glass substrates. ICDD cards 01–083–7414 for Sb_2S_3 and 01–074–9437 for Bi_2S_3 were used to identify the reflections. The reflections corresponding to the nanoribbons parallel to the substrate are marked with red rectangles, while the ones with a vertical component are marked with blue rectangles. Calculated BBXRD patterns for the end members are given as references [37,50].

completeness, several films deposited slightly outside the optimal morphology regions were additionally included to illustrate the interplay between morphology evolution and texture development.

3.1. Chemical composition of the films

XRF analysis of both thin films on glass and compressed powders was conducted to complement the EDX analysis [24] (Fig. 3). [S] values determined by means of XRF analyses are not reliable [49]. Therefore, only the [Sb]/[Bi] ratio was measured, while [S] content was suggested to be equal to the one measured by EDX in [24]. XRF results confirm the EDX findings published in [24]. With the chemical composition of the films confirmed, the focus of the investigation was directed towards the structural and textural properties of the deposited films.

3.2. In-depth texture analysis

To analyze the structural properties of the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films,

first, the BBXRD patterns were collected for both powders and films and are presented in Fig. 4. Here, the thin films with the most prominent vertical component are depicted. $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ powders and films maintain a crystal structure with the orthorhombic $Pnma$ space group symmetry, with no secondary phases detected.

To learn more about the texture of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, a set of additional techniques was applied, starting from the BBXRD-based texture coefficient (TC) and ribbon carrier transport (RCT) [51,52]. Bi_2S_3 thin films, deposited at different deposition rates (measured in nm/min), are given as an example of the protocol (Fig. 5.a). The same calculations were conducted for the five solid solutions $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ as well (Fig. 6). TC (Fig. 5.b,d) quantifies the degree of preferred orientation. Here, it is calculated according to the variation of Harris formula [53], which interprets it as a percentage [54]:

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{\sum_n I(hkl)/I_0(hkl)} \times 100\% \quad (1)$$

where the summation in the denominator is conducted for, in our case,

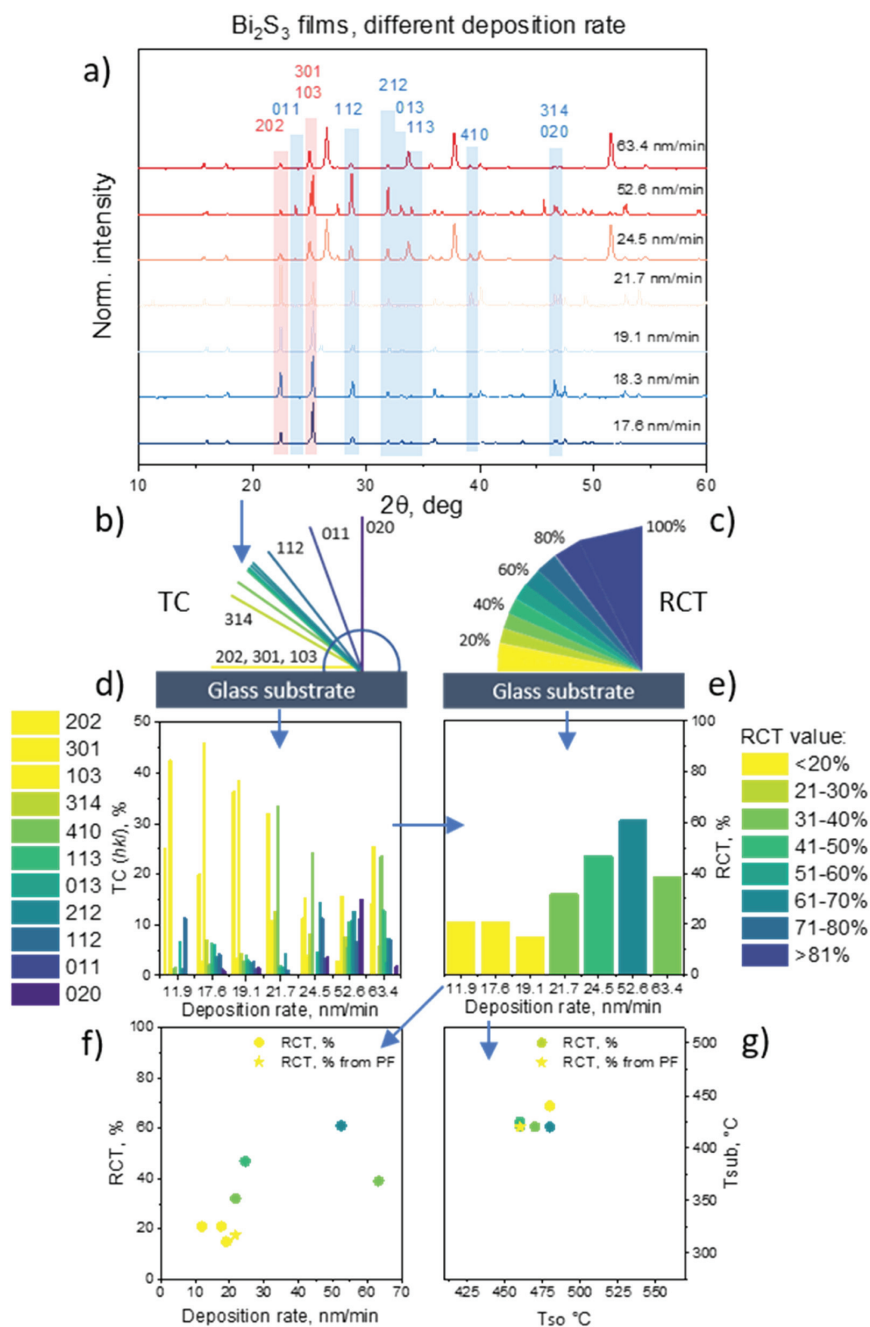


Fig. 5. An example of the protocol from BBRD data (a) to the texture information in the form of RCT. (b) Schematic diagram depicting the orientation of the nanoribbons indicated by the chosen characteristic hkl in (Sb,Bi)₂S₃ solid solutions (Pnma notation), (c) schematic diagram of the RCT values for different angles α' , (d) TC values for the chosen set of hkl reflections for each of the seven Bi₂S₃ samples, (e) the corresponding RCT values, (f) RCT values depicted against the deposition rate, (g) RCT values (colour-coded) for the corresponding deposition conditions (T_{so} and T_{sub}).

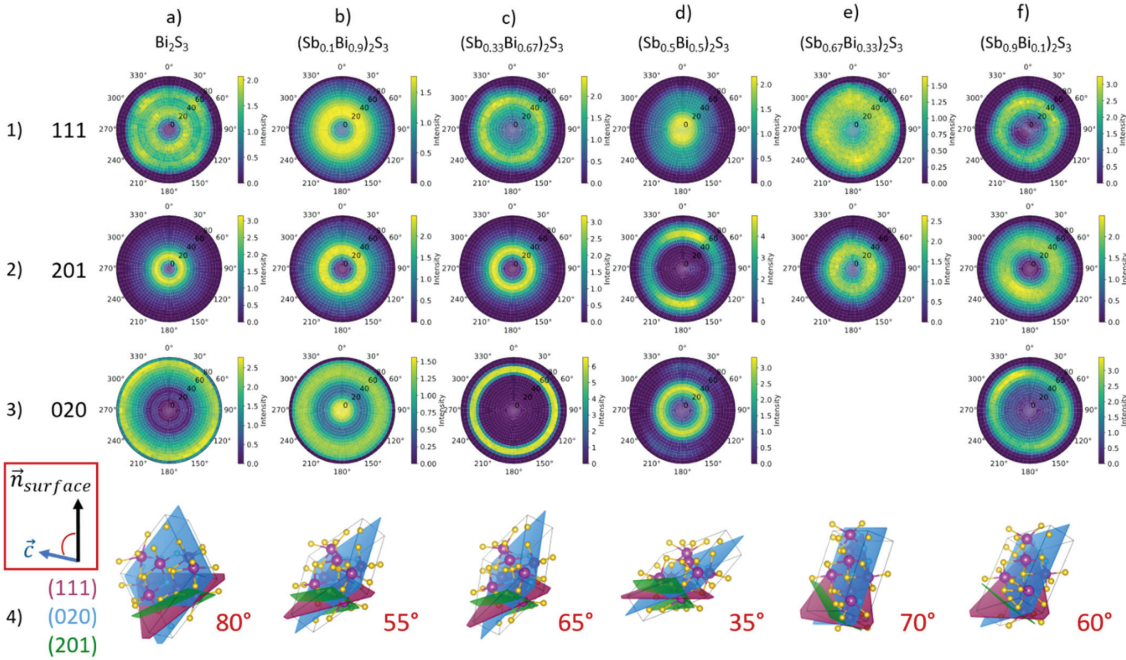


Fig. 6. Pole figures of the (1) 111, (2) 201, and (3) 020 reflections of Bi_2S_3 and $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions with (4) the resulting nanoribbon orientation (angle to substrate normal). (a – f) different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution compositions.

the $n = 10\text{--}11$ reflections, depending on the particular solid solution. Reflections were selected among the most intense ones and are highlighted in Fig. 4, namely: 202, 011, 301, 103, 112, 212, 013, 113, 410, 020 (not found in $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ patterns), 314. Reflections 202, 301, and 103 correspond to the horizontal orientation of the nanoribbons, while the 020 reflection corresponds to the vertical orientation. The relation between the lattice planes corresponding to these Bragg reflections and specific angles between the normal to the substrate and the nanoribbon orientations (angle α' , terminologically following [55]) is given in Fig. 5.b.

To describe in one number the orientation of the nanoribbons in the thin film relative to the substrate, the RCT value was calculated on the basis of the TC values [51,56]. The higher the RCT value, the more favorable the nanoribbon orientation of the quasi-1D material from the PV point of view (Fig. 5.c). According to Eq. 2, RCT is defined as:

$$RCT = \sum_n \text{TC}(hkl) \times \text{EVC}(hkl) \quad (2)$$

where n is the set of the selected hkl reflections, and EVC is an “effective vertical component,” the cosine of the angle between the nanoribbon and the substrate normal for each hkl reflection. RCT values for the Bi_2S_3 films are given in Fig. 5.e.

The RCT metric has several aspects one should consider, aiming for higher accuracy analysis:

1. It is based, by design, on a finite subset of reflections (10–11 in this work), which does not capture the full orientation distribution. In general, the reflections of the highest intensities are included in the assessment.
2. In orthorhombic materials, XRD reflections typically overlap – for example, in the Bi_2S_3 XRD pattern (ICDD 01–074–9437), the reflections 301, 103, and 111 are in close proximity at $2\theta = 24.9\text{--}25.2^\circ$, making the identification of the particular reflection

less reliable. This aspect should be considered with even higher caution in solid solutions of two orthorhombic materials, since individual reflections shift at different rates across the solid solution series and each composition produces its own unique set of overlaps.

3. There is a considerable lack of specific ICDD cards for solid solutions. For the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, ICDD cards were based on the studies [37,38], and their chemical compositions did not match the ones discussed in this work. In such cases, source material powder data may be used as references.
4. RCT is unable to distinguish a multimodal (such as a bimodal vertical + horizontal) distribution from a uniform tilted distribution of similar mean angle and is insensitive to in-plane azimuthal correlation.
5. Some characteristic reflections may not be recognizable (or not be present at all) in the analyzed pattern. As an example from this work, the 020 reflection is absent from the BBXRD pattern of $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$. In such cases, other reflections with significant vertical components may provide partial sensitivity.

Nevertheless, comparison with the pole-figure-derived tilt angle α' shows agreement in the range from 0.4° to 19.8° for all the compositions where both methods were applied (Supplementary material, Table S1), with the average and median discrepancy being 8.7° and 6.45° , respectively. The BBXRD-derived RCT is therefore used as the primary figure of merit within this study, while texture-XRD pole figures and EBSD serve as independent cross-validations.

After calculating the RCT values, it became possible to associate the verticality of the nanoribbon in the film with deposition conditions directly – namely, with deposition rate (Fig. 5.f) and the source and substrate temperatures (Fig. 5.g, RCT is coded by the color of the dots).

Texture-XRD characterization was conducted to clarify the trend in TC and RCT in $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, resulting in pole figures (PFs) in 111, 201, and 020 projections measured by XRD (Fig. 6). One film was characterized for each solid solution (plus one for Bi_2S_3). Deposition

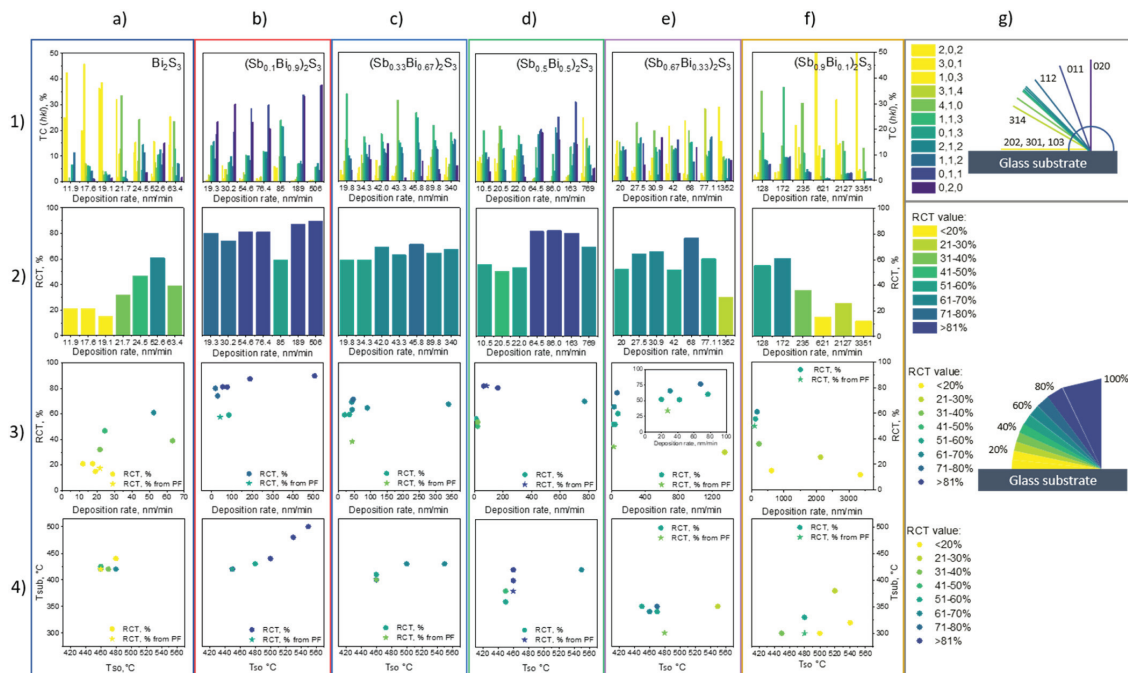


Fig. 7. Rows: (1) Texture coefficients for $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution thin films, with the reflections ordered from the ones indicating the nanoribbon growth parallel to the substrate (in yellow) to the ones indicating the nanoribbon growth perpendicular to the substrate; (2) RCT values extracted from the TC coefficients for the same samples; (3) RCT dependence on the deposition rate; (4) RCT dependence on the deposition conditions. Columns: (a)–(f) different $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solution compositions; (g) legends and visualization for TC and RCT.

conditions for the samples characterized by texture-XRD are given in the [Supplementary material, Table S2](#). The PFs are given with an intensity scale, which correlates directly with the multiple of random distribution. A larger multiple of random distribution corresponds to a more pronounced texture, which, in turn, translates into the preferred orientation [57]. Data were collected in the 0° – 85° χ range.

Asymmetry of the PFs for the samples $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ can be explained by the geometry of the sample – since the sample $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ was a quarter of the full circle, the sample $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ was one half of the full circle, and other samples were full circles. All the intensity maxima, obtained by the PFs, have the shape of a circle, with additional areas of high intensity at 90° from each other for a 111 reflection, supposedly due to the rectangular shape of the underlying substrate. For the film $(\text{Sb}_{0.67}\text{Bi}_{0.33})_2\text{S}_3$, 020 reflection was not detected. Still, the PFs were sufficient to deduce the angles α' , given in Figure 6.4.

Having characterized the texture of individual compositions, we next compare all six systems side by side to identify composition-dependent trends. The combined outcomes of the TC, RCT, and texture-XRD analysis are given in [Fig. 7](#) for Bi_2S_3 and all five $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions. Equivalents of the RCT values from the PF analysis ([Fig. 6](#)) are given in [Fig. 7.3–7.4](#) as star symbols for comparison. In [Fig. 7.1–7.3](#), TC and RCT values are given relative to the deposition rate (in nm/min) and, in [Figure 7.4](#), relative to the deposition conditions (T_{sub} , T_{so}), as in the protocol given in [Fig. 5](#).

Each data point in [Fig. 7](#) represents an independent CSS deposition; for each composition, multiple depositions were performed across the sampled (T_{so} , T_{sub}) deposition region. The scatter within each composition is dominated by the deposition rate variation, as reflected in the strong RCT versus deposition rate correlations in [Figures 7.1–7.4](#).

Calculated TC values for the $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions thin films

deposited at various deposition rates are presented in [Figure 7.1](#). The highest deposition rate typically corresponds to the higher T_{so} and a greater difference between T_{so} and T_{sub} . At deposition rates higher than those included in this study, Bi_2S_3 and Bi-rich solid solutions, instead of densely-packed thin films, form agglomerations of randomly-oriented needle-like and leaf-like structures, while Sb_2S_3 and Sb-rich solid solutions form scale-like grains with horizontal nanoribbon orientation [15, 24]. Due to the higher vapor pressure of Sb_2S_3 [24], Sb-rich solid solutions have a higher deposition rate under the same deposition conditions. For Bi_2S_3 thin films ([Figure 7.1.a](#)), reflections 202, 301, and 103 (corresponding to the lateral orientation of nanoribbons) are the most prominent at a deposition rate below 20–24 nm/min, corresponding to the $T_{\text{so}} < 480^\circ\text{C}$ and $T_{\text{sub}} > 420^\circ\text{C}$ and, therefore, a ΔT below 60°C . Reflections with the higher vertical component (especially 011 and 020) are present only at a 53 nm/min deposition rate ($T_{\text{so}} = 480^\circ\text{C}$, $T_{\text{sub}} = 420^\circ\text{C}$). Surprisingly, $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ solid solution thin films ([Figure 7.1.b](#)) have the most pronounced 011 and 020 reflections among all the studied $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ systems, while the presence of the lateral component (202, 301, and 103 reflections) was very limited.

At the deposition rates above 180 nm/min, which correspond to $T_{\text{sub}} = 480$ – 500°C and $T_{\text{so}} = 500$ – 550°C , especially pronounced 011 and 020 reflections were found. However, under these conditions, deposited films had uneven morphology, with the partial re-evaporation and the formation of spikes and voids instead of a dense film ([Supplementary material, Figure S1](#)). In $(\text{Sb}_{0.33}\text{Bi}_{0.67})_2\text{S}_3$ thin films ([Figure 7.1.c](#)), the most pronounced reflections were 410, 113, and 013. For $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ thin films ([Figure 7.1.d](#)), two distinct deposition rate regions were identified. For the deposition rates up to 21 nm/min ($T_{\text{so}} < 460^\circ\text{C}$), the most pronounced reflections were 410, 113, and 013, while the reflections 011 and 020 were moderate. However, at deposition rates of 60–165 nm/min ($T_{\text{so}} > 460^\circ\text{C}$), the reflections with a higher vertical

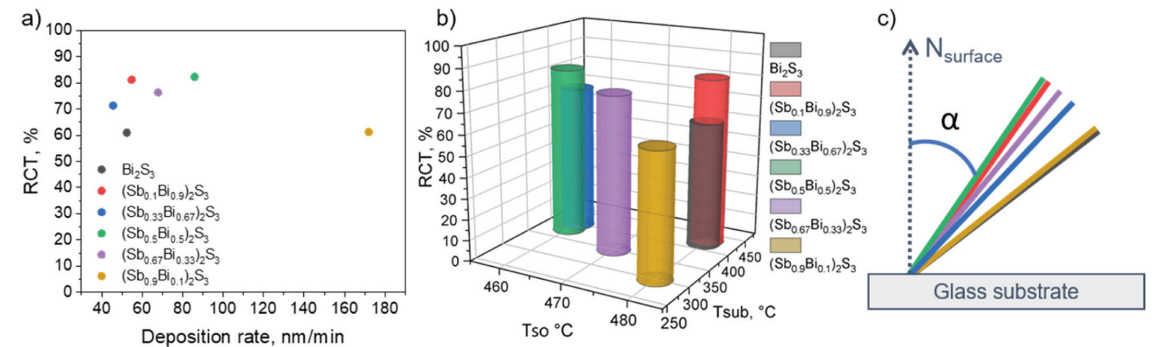


Fig. 8. Deposition rates (a) and deposition conditions (b) for the CSS-deposited thin films from (Sb_xBi_{1-x})₂S₃ solid solutions on glass substrates with the highest RCT value, (c) visualization of the optimized nanoribbon orientations (smallest angles α') for all (Sb_xBi_{1-x})₂S₃ systems.

component (011, 020) dominated, dropping again for the reference sample with $T_{so} = 550$ °C. From Bi₂S₃ up to (Sb_{0.5}Bi_{0.5})₂S₃, the typical pattern was the same – stronger lateral components at lower deposition rates, stronger vertical components at higher deposition rates. For (Sb_{0.67}Bi_{0.33})₂S₃ (Figure 7.1.e), increasing deposition rate corresponded to the decreasing intensity of reflections with a bigger vertical component, while the reflections 202, 301, and 314 were getting more prominent for the deposition rates above 42 nm/min ($T_{so} > 470$ °C and $T_{sub} = 340$ –350 °C). For (Sb_{0.9}Bi_{0.1})₂S₃ (Figure 7.1.f), the pattern typical for Bi-rich solid solutions was fully inverted: at the lowest applied deposition rates (128–172 nm/min, with $T_{so} = 480$ °C and $T_{sub} = 300$ –330 °C), the most pronounced reflections were 410 and 113, with a considerable intensity of higher vertical component reflections as well. But at the higher deposition rates ($T_{so} > 480$ °C and $T_{sub} = 300$ –380 °C), the lateral component overwhelmingly dominates, indicating that the nanoribbons grow mostly parallel to the substrate surface.

When comparing the (Sb_xBi_{1-x})₂S₃ systems with each other, the contribution of 020 and 011 reflections increases with the deposition rate for the Bi-rich solid solutions up to (Sb_{0.5}Bi_{0.5})₂S₃, and decreases for Sb-rich solid solutions. At the extremely high deposition rates (from 504 nm/min for (Sb_{0.1}Bi_{0.9})₂S₃ to 3351 nm/min for (Sb_{0.9}Bi_{0.1})₂S₃), the higher share of Sb in the solid solution corresponded to the higher lateral and smaller vertical components.

RCT values, calculated from the TC in Figure 7.1, are given in Figure 7.2. Here, the patterns discussed in terms of the TCs are more visible. RCT values relative to a deposition rate on a linear scale are given in Figure 7.3. Cosines of the angles α' derived from the texture-XRD (Fig. 6), being interpreted as %, give the same information as RCT and are shown in Figures 7.3 and 7.4 as star symbols. In most cases (with one exception of (Sb_{0.9}Bi_{0.1})₂S₃), the PF-derived α' values were larger (more lateral nanoribbon orientation) than the BBXRD-derived ones (Supplementary material, Table S1). This offset is consistent with the aspects of the BBXRD-TC-RCT pipeline in orthorhombic solid solutions, discussed above. Defocusing corrections at high χ in pole-figure measurements [58,59] may be a minor additional contributor. Overall, the PF-derived data support the texture trend observed from BBXRD.

The data show that Bi₂S₃ nanoribbons are lying almost parallel to the substrate at low (below 20 nm/min) deposition rates, with the highest RCT of 60.9% obtained at a 53 nm/min deposition rate ($T_{so} = 480$ °C, $T_{sub} = 420$ °C). At the same time, most (Sb_{0.1}Bi_{0.9})₂S₃, (Sb_{0.33}Bi_{0.67})₂S₃, and (Sb_{0.5}Bi_{0.5})₂S₃ samples had RCT values of 55% and higher. Thus, adding 10 at% Sb₂S₃ already altered the depositional behavior of the solid solution compared to pure Bi₂S₃. This change at only 10 at% Sb₂S₃ substitution cannot be attributed to a kinetic supersaturation shift, since log10(supersaturation) is essentially the same (0.7–1.6) for Bi₂S₃ and (Sb_{0.1}Bi_{0.9})₂S₃ [24]; the composition-driven structural origins of this observation are discussed in Section 3.3. For the growth of vertically

Table 2
Deposition rates, T_{so} , T_{sub} , RCT, and the angles α' for the CSS-deposited thin films from (Sb_xBi_{1-x})₂S₃ solid solutions on glass substrates with the most vertical nanoribbon orientation.

Material	T_{so} , °C	T_{sub} , °C	DepRate, nm/min	RCT, %	Angle α' , deg.
Bi ₂ S ₃	480	420	53	60.9	52.5
(Sb _{0.1} Bi _{0.9}) ₂ S ₃	480	430	55	81.1	35.8
(Sb _{0.33} Bi _{0.67}) ₂ S ₃	460	400	46	71.3	44.5
(Sb _{0.5} Bi _{0.5}) ₂ S ₃	460	380	86	82.3	34.6
(Sb _{0.67} Bi _{0.33}) ₂ S ₃	470	350	68	76.4	40.2
(Sb _{0.9} Bi _{0.1}) ₂ S ₃	480	300	172	61.2	52.3

oriented nanoribbons of (Sb_{0.5}Bi_{0.5})₂S₃ solid solution, the deposition rate in the region 60–160 nm/min is preferred, with an optimal rate of 86 nm/min (corresponding to $T_{so} = 460$ °C, $T_{sub} = 380$ °C), leading to the RCT value of 82.3%, while at lower deposition rates (lower T_{so} or higher T_{sub}), the films exhibit an RCT no higher than 56%. (Sb_{0.67}Bi_{0.33})₂S₃ nanoribbons are generally less perpendicular to the substrate compared with more Bi-rich solid solutions, and their RCT decreases as the deposition rate increases. (Sb_{0.9}Bi_{0.1})₂S₃ continues the tendency, which started from (Sb_{0.67}Bi_{0.33})₂S₃, with higher RCT values at lower deposition rates.

RCT values (colour-coded) relative to the deposition conditions (T_{so} , T_{sub}) are given in Figure 7.4. For all the solid solutions, RCT values higher than 60% (dark-green and blue dots) were achieved via deposition in the region of $T_{sub} = 290$ –420 °C and $T_{so} = 450$ –480 °C. Based on the preceding analysis, the deposition rate and conditions for the densely-packed thin films with the highest RCT values are given in Fig. 8 and Table 2. The deposition conditions follow the general trend outlined in [24].

The deposition conditions for the thin films with the highest BBXRD-derived RCT values (correspondingly, smallest α') among the ones in the Fig. 7, which also maintained densely-packed morphology, are given in Table 2 and Fig. 8. The notable exceptions are the highly textured, but not densely-packed (Sb_{0.1}Bi_{0.9})₂S₃ films, deposited at higher-than-optimal T_{sub} (Figure S1). The densely-packed (Sb_{0.5}Bi_{0.5})₂S₃ and (Sb_{0.1}Bi_{0.9})₂S₃ films had the highest RCT of 82.3% and 81.1%, corresponding to the smallest α' of 34.6° and 35.8°, respectively, among all the characterized samples.

3.3. On the origin of the composition-dependent texture tendencies

The composition-dependent texture evolution observed across the CSS-deposited (Sb_xBi_{1-x})₂S₃ series is proposed to originate from the interplay between deposition kinetics during thin-film growth/formation [24] and the intrinsic degree of structural anisotropy of each solid

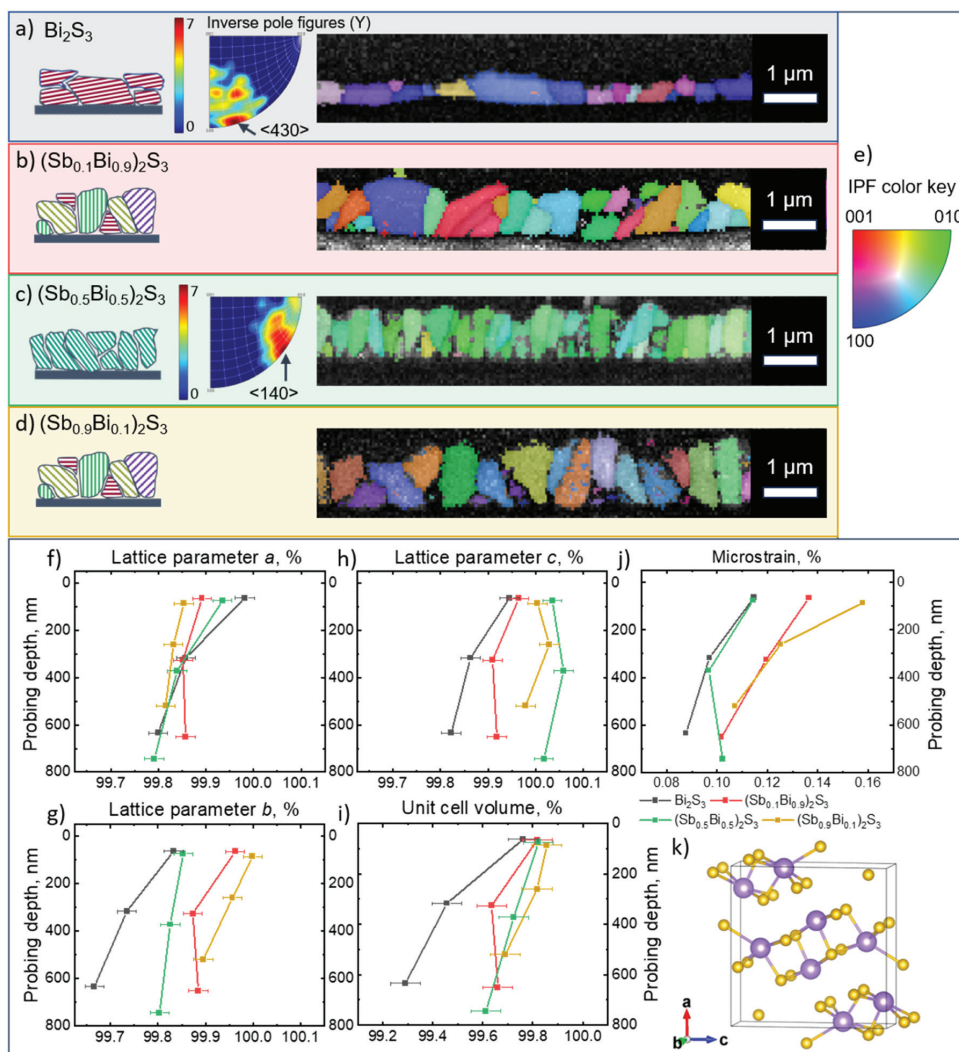


Fig. 9. Texture-structure relations in CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films. (a-d) Texture information for four thin films with the (a) most lateral, (c) most vertical and (b,d) disordered orientation of nanoribbons among the grains, including the inverse pole figures (IPF) for Y axis (the colors representing the multiples of random distribution) and EBSD cross-sections, with (e) an IPF color key; (f-i) relative change in lattice parameters and $V_{\text{unit cell}}$; (j) change in microstrain, and (k) a schematic depiction of a $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ unit cell with corresponding vectors in Pnma notation [24].

solution [37]. In our previous study [24], the deposition-regime protocol for CSS-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films was established, identifying the optimal substrate and source temperatures required for obtaining dense, continuous, and morphologically suitable films across the composition range. Within the present study, primarily thin films deposited within these morphology-compatible growth windows were selected for texture analysis.

As demonstrated by Kyono and Kimata [37], progressive substitution of Bi^{3+} by Sb^{3+} increases the stereoactivity of the ns^2 lone-pair electrons, producing increasingly distorted M-S coordination polyhedra and enhancing the bonding anisotropy of the orthorhombic stibnite-bismuthinite structure. This distortion strengthens the contrast between the strong covalent bonding along the nanoribbon axis (b -axis) and the weaker inter-ribbon interactions along the a and c directions. Consequently, the intrinsic growth-rate anisotropy progressively

increases with Sb incorporation, promoting preferential elongation along the ribbon axis during crystal growth. During CSS deposition (at an established optimized deposition regime (OGR) [24]), this intrinsic anisotropy interacts with supersaturation-dependent nucleation density and adatom mobility. Under moderate supersaturation and sufficiently high substrate temperatures, adatom mobility remains high enough to promote grain coalescence and competitive growth between differently oriented crystallites/nanoribbons. Under such conditions, evolution-selection mechanisms favour grains whose nanoribbon axis becomes preferentially aligned closer to the substrate normal, leading to enhanced vertical texture and higher RCT values [60].

This can be a suitable framework to explain the experimentally observed composition-dependent behaviour. In Bi-rich compositions, despite relatively high substrate temperatures favourable for surface diffusion, the intrinsic growth-rate anisotropy remains comparatively

Table 3
Outcomes of the three different ways to assess the angles between the nanoribbon and the substrate normal (BBXRD, PF, EBSD).

Sample	BBXRD-derived		PF-derived		EBSD-derived	
	Angle α' , deg.	RCT, %	Angle α' , deg.	RCT, %	Angle α' , deg.	RCT, %
Bi_2S_3	71.33	32.00	80.00	17.36	74.00	27.56
$(Sb_{0.1}Bi_{0.9})_2S_3$	50.80	63.20	55.00	57.36	NaN	NaN
$(Sb_{0.5}Bi_{0.5})_2S_3$	34.60	82.30	35.00	81.91	36.00	80.90
$(Sb_{0.9}Bi_{0.1})_2S_3$	62.50	46.44	60.00	50.00	NaN	NaN

weak due to the limited stereoactivity of the Bi lone pair, resulting in only modest texture evolution. Already at modest Sb incorporation, however, the enhanced lone-pair stereoactivity significantly sharpens the bonding anisotropy and strengthens orientation-selection tendencies. This effect appears particularly pronounced for $(Sb_{0.1}Bi_{0.9})_2S_3$, where only 10 at% Sb incorporation already leads to a substantial improvement in texture, yielding RCT $\approx 81.1\%$ and $\alpha' \approx 36^\circ$. Such behaviour suggests that even modest Sb incorporation is sufficient to noticeably perturb the local coordination geometry and enhance the intrinsic growth-rate anisotropy of the system. Additionally, our previous Raman analysis [24] revealed a weak Sb_2S_3 -related vibrational contribution in $(Sb_{0.1}Bi_{0.9})_2S_3$, which may indicate subtle local structural or surface-related heterogeneity additionally influencing the growth behaviour. The most favourable texture is observed for $(Sb_{0.5}Bi_{0.5})_2S_3$, where the intrinsic growth anisotropy is sufficiently strong to drive preferential orientation while substrate temperatures remain high enough for effective grain coalescence and orientation evolution.

In contrast, Sb-rich compositions require substantially lower substrate temperatures and higher supersaturation conditions to maintain dense and continuous film growth [24]. Although these compositions possess intrinsically stronger structural anisotropy, the lower substrate temperatures reduce adatom mobility, while the higher supersaturation increases nucleation density. Under these kinetically constrained conditions, grain coalescence and orientation-selection processes become increasingly hindered, suppressing the development of highly vertical texture despite the stronger intrinsic anisotropy of the crystal structure.

Because all films in the present study were deposited on amorphous soda-lime glass substrates, epitaxial lattice-matching effects are not expected to play a dominant role in the observed texture evolution. Instead, the results suggest that the nanoribbon orientation is governed primarily by the interplay between composition-dependent crystal-chemical anisotropy and deposition kinetics during CSS thin-film growth.

3.4. EBSD cross-evaluation of the RCT and texture-XRD findings

To independently verify the findings derived from BBXRD and texture-XRD, and to resolve the texture information at the level of individual grains, EBSD orientation mapping was conducted for the samples, which were previously examined through BBXRD (with calculation of TC and RCT) and texture-XRD. The cross-sectional EBSD maps of four samples (Bi_2S_3 , $(Sb_{0.1}Bi_{0.9})_2S_3$, $(Sb_{0.5}Bi_{0.5})_2S_3$, and $(Sb_{0.9}Bi_{0.1})_2S_3$) are shown in Fig. 9.a-d. The observed $(Sb_{0.1}Bi_{0.9})_2S_3$ and $(Sb_{0.9}Bi_{0.1})_2S_3$ grains are larger than those of $(Sb_{0.5}Bi_{0.5})_2S_3$. It is evident that the

Table 4
Difference between the biggest and the smallest value among the GIXRD-derived lattice parameters, $V_{unit\ cell}$, and microstrain for the four CSS-deposited $(Sb_xBi_{1-x})_2S_3$ thin films for which EBSD texture assessment was available, with the biggest differences highlighted in bold.

	Texture	Δa , %	Δb , %	Δc , %	ΔV , %	$\Delta MicSt$, %
Bi_2S_3	horizontal	0.0018	0.0017	0.0012	0.0047	0.0270
$(Sb_{0.1}Bi_{0.9})_2S_3$	none	0.0003	0.0009	0.0005	0.0018	0.0345
$(Sb_{0.5}Bi_{0.5})_2S_3$	vertical	0.0014	0.0005	0.0004	0.0021	0.0176
$(Sb_{0.9}Bi_{0.1})_2S_3$	none	0.0004	0.0010	0.0005	0.0017	0.0509

nanoribbon orientation in the Bi_2S_3 thin films is mostly parallel to the substrate surface, and that in $(Sb_{0.1}Bi_{0.9})_2S_3$ and $(Sb_{0.9}Bi_{0.1})_2S_3$ thin films there is a significant variety of the nanoribbon orientations among the grains, which makes it harder to discuss the preferred orientation and explains the especially dispersed PFs (see Fig. 6.b,f). However, the $(Sb_{0.5}Bi_{0.5})_2S_3$ thin film exhibits a profound preferential vertical nanoribbon orientation and consists of the densely-packed columnar grains. It is in agreement with BBXRD-derived RCT and PF-derived RCT (Table 3), with all three methods showing the angles α' with an agreement of $1.4\text{--}8.7^\circ$.

3.5. Structural depth profiling (GIXRD)

While the preceding analysis addressed the preferential orientation of nanoribbons in the films, a complementary question concerns the evolution of the crystal structure itself – specifically, whether the lattice parameters and microstrain vary through the film thickness. To address this, GIXRD depth profiling was conducted, focusing on three probing zones of the film ($<65\text{--}85\text{ nm}$, $<240\text{--}370\text{ nm}$, and $<475\text{--}750\text{ nm}$), as outlined in Section 2.2. One sample from each $(Sb_xBi_{1-x})_2S_3$ system was characterized, using the same samples that were also characterized by texture-XRD (deposition conditions are given in Table S2), with similar thickness and compatible roughness (Fig. 6 in [24]).

An illustration of the working principle of GIXRD profiling, along with a set of initial GIXRD graphs, is provided in the Supplementary material (Figures S2 and S3, respectively). The main information extracted from the GIXRD data included the change in lattice parameters, and, consequently, the unit cell volume ($V_{unit\ cell}$), as well as the microstrain through depth of the thin film [61] (three characterized probing zones). Since all compositions share the same space group and have similar diffraction patterns, Le Bail fitting biases are expected to be systematic and largely uniform across the dataset, and are therefore unlikely to account for the composition-dependent ordering of Δa , Δb , and Δc reported in Table 4. The microstrain was determined using the Stokes-Wilson equation, with integral peak breadths (corrected for the instrumental broadening using the Thompson-Cox-Hastings pseudo-Voigt function) used as peak width parameter [62,63]. The comparison among the six analyzed thin films is shown in Fig. 10. Lattice parameters and $V_{unit\ cell}$ are both compared as absolute values (Fig. 10.a-d) and as a percentage of the reference (powder samples of the corresponding solid solutions) (Fig. 10.e-h).

To assess the probability of the depth-related changes in chemical composition as the reason for the structural changes, the EDX mapping was conducted for the same samples as EBSD (Supplementary material, Figure S4). In samples $(Sb_{0.5}Bi_{0.5})_2S_3$ and $(Sb_{0.9}Bi_{0.1})_2S_3$, the anomalies in chemical composition were indeed found:

- In the $(Sb_{0.5}Bi_{0.5})_2S_3$ sample, a layer of slightly Sb-rich and Bi-poor composition was found at the surface of the film;
- In the $(Sb_{0.9}Bi_{0.1})_2S_3$ sample, a region with Sb-rich and S-poor composition was found near the substrate of the film.

At the same time, the chemical composition profiling of the samples Bi_2S_3 and $(Sb_{0.1}Bi_{0.9})_2S_3$ revealed no compositional gradients or anomalies, despite the similar changes in lattice parameters and microstrain. Therefore, the chemical composition could not be recognized as the sole

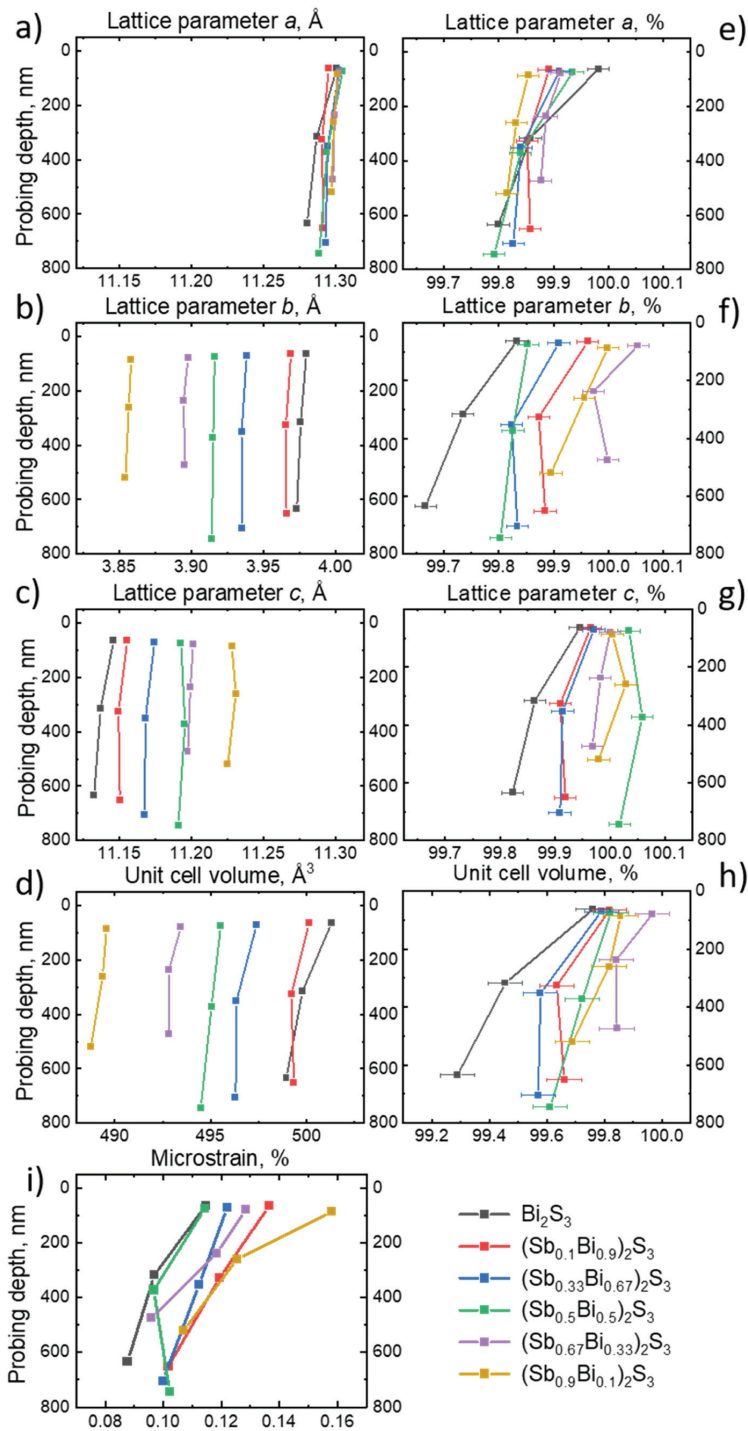


Fig. 10. Change in lattice parameters, unit cell volume, and microstrain in CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films, given against the probing depth. Lattice parameters and unit cell volume are given in (a-d) absolute values and (e-h) relative to the powder reference values, while (i) microstrain is always quantified in percent.

reason for the detected depth-related structure changes.

Because b spans 4.3% across the full solid-solution series while a and c change by less than 1% [37], the absolute values in Fig. 10.b cleanly separate the six compositions but obscure the depth-dependent signal within each. The relative representation (Fig. 10.e–h), normalized to the powder reference of each composition, filters out this composition baseline and reveals the depth-dependent strain on a common scale.

On this scale, the depth-dependent variation of individual lattice parameters correlates with texture (Fig. 9, Table 4): in the three films where b is not perpendicular to the substrate – Bi_2S_3 (horizontal texture), $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ (no texture) – b shows the largest or co-largest relative depth variation. In the vertically textured $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$, where b is oriented normal to the substrate and therefore unconstrained, a – the inter-ribbon direction, now in-plane – takes over as the parameter with the largest depth-related variation. At the same time, the highest degree of microstrain aggregation from substrate to surface (Fig. 10.i) was found in the $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ and $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ films with no texture, and in the $(\text{Sb}_{0.9}\text{Bi}_{0.1})_2\text{S}_3$ film, it aggregates more than in $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$. This correlation between depth-dependent lattice parameter changes and nanoribbon orientation may reflect residual stress at the film–substrate interface, though the present GIXRD data do not allow direct stress quantification, and other contributions cannot be excluded.

Another reason for such changes in unit cell parameters may be differences in the growth processes for vertically and horizontally oriented nanoribbons. Vertically oriented nanoribbons are limited in their growth – they must grow upward, with only rotation along the long axis [64] and some nanoribbon bending [65] as possible deviations, which may limit the possible changes in lattice parameters as well. In the case of the horizontally-oriented nanoribbons, they have at least one additional "degree of freedom": nanoribbons, deposited atop each other, may show a behavior similar to turbostratic disorder in 2D materials. For graphene [66] and MoS_2 [67], it leads to a slight increase in interlayer distances, and for quasi-one-dimensional materials, such as $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$, it may have a similar effect. Still, more research is needed in this particular area to draw stronger conclusions.

Overall, this study provides a platform for future research on the structure-related deposition of $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin films by physical methods. For each solid solution, a texture baseline was established, which may be further improved by optimizing deposition conditions, introducing post-deposition procedures, or using other substrates/ETLs that may promote particular nanoribbon growth directions. While $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ and more Sb-rich materials are p-type and may be used with classic ETLs such as TiO_2 and CdS , Bi-rich materials, being n-type, provide additional challenges in band alignment engineering. Beyond the thin-film solar cells research, the BBXRD-TC-RCT texture analysis methodology and its cross-check by texture-XRD and EBSD, implemented in this study, may be found useful in the broader application range, including photocatalysis and other optoelectronic applications.

4. Conclusions

This work provides the first systematic mapping of nanoribbon orientation in CSS-deposited $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ ($0 \leq x \leq 0.9$) thin films across a broad compositional range, establishing qualitative and quantitative correlations between deposition conditions and texture evolution. The combined BBXRD-TC-RCT, texture-XRD, and EBSD analyses consistently identify $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ as the composition exhibiting the most favourable texture within the investigated process window on soda-lime glass, achieving $\text{RCT} = 82.3\%$ and $\alpha' \approx 35^\circ$ at $T_{\text{so}} = 460^\circ\text{C}$ and $T_{\text{sub}} = 380^\circ\text{C}$. In contrast, both Bi-rich and Sb-rich compositions favour more lateral nanoribbon orientations. Although densely-packed $(\text{Sb}_{0.1}\text{Bi}_{0.9})_2\text{S}_3$ films also exhibit comparably high RCT values ($\approx 81.1\%$), the combined texture, EBSD, and morphology analysis suggests that $(\text{Sb}_{0.5}\text{Bi}_{0.5})_2\text{S}_3$ provides the most balanced structural characteristics within the investigated process window. GIXRD depth profiling reveals that the depth-dependent evolution of lattice parameters and microstrain correlates

with nanoribbon orientation, while non-textured films exhibit the strongest microstrain aggregation. A possible mechanism for the composition-dependent texture evolution is proposed, suggesting that the observed texture behaviour originates from the interplay between deposition kinetics and the composition-dependent structural anisotropy of the orthorhombic solid solutions, probably driven by the progressive increase in Sb lone-pair stereoactivity. Overall, this study establishes a texture-versus-process framework for CSS-grown $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid solutions and provides a structural foundation for future device-oriented optimization on technologically relevant substrates and interfaces.

CRedit authorship contribution statement

Mykhailo Koltsov: Conceptualization, Investigation, Validation, Methodology, Formal analysis, Data curation, Writing – original draft, Writing – review & editing, Visualization. **René Schwidessen:** Investigation, Validation, Methodology, Formal analysis, Data curation, Writing – review & editing. **Daniel Abou-Ras:** Investigation, Formal analysis, Validation, Data curation, Writing – review & editing. **Susan Schorr:** Formal analysis, Validation, Methodology, Writing – review & editing, Visualization. **Ilona Oja Acik:** Funding acquisition, Project administration, Validation, Writing – review & editing. **Nicolae Spalatu:** Conceptualization, Funding acquisition, Project administration, Validation, Methodology, Data curation, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ilona Oja Acik reports financial support was provided by Estonian Research Council. Ilona Oja Acik reports financial support was provided by Estonian Ministry of Education and Research. Ilona Oja Acik reports financial support was provided by Horizon 2020 European Innovation Council Fast Track to Innovation. Nicolae Spalatu reports financial support was provided by European Cooperation in Science and Technology. If there are other authors, they 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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the

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2024 Oral presentation on EMRS Fall Meeting, 16-19.09.2024, in Warsaw, Poland.

- 2024 Poster presentation on 14th European Kesterite+ RenewPV Workshop, 26-28.06.2024, in Verona, Italy.
- 2024 Participation in the Advanced School for X-ray Diffraction, 27-31.05.2024, in Berlin, Germany.
- 2024 Participation in Quantsol winter school, 9-14.01.2024, in Hirschegg, Austria.
- 2023 Oral presentation on Kesterite workshop in Barcelona, 5-7.07.2023, Barcelona, Spain.
- 2023 Poster presentation on 1st International Workshop on Emerging Inorganic Chalcogenides Photovoltaics, 15-16.06.23, Tallinn, Estonia.
- 2023 Poster presentation on Luxembourg Space Resources Week, 19-21.04.2023, Luxembourg.
- 2022 Poster presentation on Röntgen-Ångström International Summer School 2022, 14-21.08.2022, Varberg, Sweden.
- 2022 Poster presentation on SeeFuturePV conference, 22-24.06.2022, Lausanne, Switzerland.
- 2022 Online poster presentation on EMRS spring meeting, 30.05-02.06.2022.
- 2022 Poster presentation on GSFMT conference, 17-18.05.2022, Tallinn, Estonia.

Supervised dissertations

Makar Ivashko, Bachelor student, (sup) Martin Eerme; Mykhailo Koltsov, Arduino-based automation system for close-spaced sublimation, Tallinn University of Technology, 2023.
 Ivan Pavlov, Bachelor student, (sup) Mykhailo Koltsov, Development of the close-spaced sublimation reactor with the external cooling and substrate spinning systems, Tallinn University of Technology, 2025.

Research projects

1. **PRG627**, Antimony chalcogenide thin films for next generation semi-transparent solar cells applicable in electricity producing windows.
2. **PSG689**, Bismuth chalcogenide thin film disruptive green solar technology for next generation photovoltaics.
3. **TK210U8**, GREENTECH.
4. **CA21148**, Research and International Networking on Emerging Inorganic Chalcogenides for Photovoltaics.
5. **MOB3PRT17**, Sustainable chalcogenide thin films for low power photovoltaics.
6. **PRG2676**, All inorganic semi-transparent thin film solar cells for solar windows and indoor photovoltaics.
7. **101183049**, Solar Cells-Inspired Inorganic Semiconductor Synaptic Systems for Low Energy Edge Computing and Visual Learning.

List of publications

1. **M.A. Koltsov**, R. Schwiddessen, D. Abou-Ras, S. Schorr, I. Oja Acik, and N. Spalatu. (2026). "Understanding the correlation between deposition conditions and nanoribbon orientation in close-spaced sublimated $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ thin film solid solutions", Journal of Alloys and Compounds, 1073, 189037, 2026, DOI: 10.1016/j.jallcom.2026.189037
2. **M.A. Koltsov**; G. Colibaba; D. Miliaieva; E. Dudutienė; M. Guc; V. Rotaru; D. Untila; J. Hiie; M. Krunk; I. Oja Acik; N. Spalatu. (2026). Composition-tunable $(\text{Sb}_x\text{Bi}_{1-x})_2\text{S}_3$ solid-solution thin films via close-spaced sublimation. Journal of

- Alloys and Compounds, 1065, ARTN 188010. DOI: 10.1016/j.jallcom.2026.188010.
3. D. Milišević; V. Nádaždy; **M.A. Koltsov**; C. López; H. Saeeyekta; J. Kuliček; C. Cazorla; E. Saucedo; R. Grzibovskis; A. Vembris; M. Krunk; B. Rezek; N. Spalatu. (2025). Electronic structure and defect states in bismuth and antimony sulphides identified by energy-resolved electrochemical impedance spectroscopy. *Journal of Physics Energy*, 7, 3, #035012. DOI: 10.1088/2515-7655/add59f.
 4. Drabavičius, A.; Pakštas, V.; Jasiūnas, R.; **Koltsov, M.**; Talaikis, M.; Naujokaitis, A.; Spalatu, N.; Kondrotas, R.; Gulbinas, V.; Franckevičius, M. (2025). Synthesis and characterization of polycrystalline GeS thin films for optoelectronic applications. *Materials Science in Semiconductor Processing*, 188, #109193. DOI: 10.1016/j.mssp.2024.109193.
 5. Colibaba, G.V.; Rusnac, D.; Fedorov, V.; **Koltsov, M. A.**; Volobujeva, O.; Grzibovskis, R.; Vembris, A.; Spalatu, N. (2024). ZnO thin films co-doped with III-valence metals and halogens: theory and experiment. *Physica Scripta*, 99, 10, #105967. DOI: 10.1088/1402-4896/ad74ab.
 6. **Koltsov, M.**; Gopi, S.V.; Raadik, T.; Krustok, J.; Josepson, R.; Grzibovskis, R.; Vembris, A.; Spalatu, N. (2023). Development of Bi₂S₃ thin film solar cells by close-spaced sublimation and analysis of absorber bulk defects via in-depth photoluminescence analysis. *Solar Energy Materials and Solar Cells*, 254, #112292. DOI: 10.1016/j.solmat.2023.112292.
 7. **Koltsov, M.**; Krautmann, R.; Katerski, A.; Maticiu, N.; Krunk, M.; Oja Acik, I.; Spalatu, N. (2022). A Post-deposition annealing approach for organic residues control in TiO₂ and its impact on Sb₂Se₃/TiO₂ device performance. *Faraday Discussions*, 239, 273–286. DOI: /10.1039/D2FD00064D.

Elulookirjeldus

Isikuandmed

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Haridus

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2019 - 2021 Tallinna Tehnikaülikool + Tartu Ülikool
Materjalid ja protsessid jätkusuutlikus energeetikas, MSc cum laude
2016 - 2018 National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»
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2012 - 2016 National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»
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Keeleoskus

Ukraina keel – emakeel
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Töökogemus

2021 - 2026 Õhukestekilelistekilede energiamaterjalide teaduslabor, Tallinna Tehnikaülikool, nooremteadur.
2017-2018 Resource Efficient and Cleaner Production Centre, Ukraina, praktikant.

Konverentsidel ja suvekoolides osalemine

2026 Summer School "Light-Activated Materials for Emerging Applications", 6-9.07.2026. Poster ettekanne.
2026 4th ReNewPV + 16th European Kesterite Conference, 17-19.06.2026. Poster ettekanne.
2025 ICPAM-17 conference, 16-23.11.2025. E-poster ettekanne.
2025 Next Generation High Efficiency Photovoltaics International School and Workshop 2025 (NEXTGEN), 08-12.09.2025, Palma de Mallorca, Hispaania. Poster ettekanne.
2025 MicroTherm'2025 conference, 23-25.06.2025, Łódź, Poland. Suuline ettekanne.
2025 Luxembourg Space Resources Week, 19-21.05.2025, Luksemburg. Poster ettekanne.
2024 EMRS Fall Meeting, 16-19.09.2024, Varssavi, Poola. Suuline ettekanne.
2024 14th European Kesterite+ RenewPV Workshop, 26-28.06.2024, Verona, Itaalia. Poster ettekanne.
2024 Advanced School for X-ray Diffraction, 27-31.05.2024, Berliin, Saksamaa. Osaleja.

- 2024 Quantsol winter school, 9-14.01.2024, Hircheegg, Austria. Osaleja.
- 2023 Kesterite workshop, 5-7.07.2023, Barcelona, Hispaania. Suuline ettekanne.
- 2023 1st International Workshop on Emerging Inorganic Chalcogenides Photovoltaics, 15-16.06.23, Tallinn, Eesti. Poster ettekanne.
- 2023 Luxembourg Space Resources Week, 19-21.04.2023, Luksemburg. Poster ettekanne.
- 2022 Röntgen-Ångström International Summer School 2022, 14-21.08.2022, Varberg, Rootsi. Poster ettekanne.
- 2022 SeeFuturePV conference, 22-24.06.2022, Lausanne, Šveits. Poster ettekanne.
- 2022 EMRS spring meeting, 30.05-02.06.2022. E-poster ettekanne.
- 2022 Graduate School of Functional Materials and Technologies (GSFMT), 17-18.05.2022, Tallinn, Eesti. Poster ettekanne.

Supervised dissertations

Makar Ivashko, bakalaureusekraad, (juh) Martin Eerme; Mykhailo Koltsov, "Arduino-põhine automaatikasüsteem suletud ruumi sublimatsiooniks", Tallinna Tehnikaülikool, 2023.

Ivan Pavlov, bakalaureusekraad, (juh) Mykhailo Koltsov, "Välise jahutuse ja substraadi pöörlemissüsteemidega lähispinnalise sublimatsioonireaktori arendamine", Tallinna Tehnikaülikool, 2025.

Teadusprojektid

1. **PRG627**, Antimon-kalkogeniid õhukesed kiled järgmise põlvkonna pool-läbipaistvatele päikeseelementidele kasutamiseks elektrit tootvates akendes.
2. **PSG689**, Õhukesekilelised vismutkalkogeniidid murrangulisele tulevase põlvkonna päikeseenergiatehnoloogiale.
3. **TK210U8**, Jätkusuutliku rohevesiniku ja energiatehnoloogia tippkeskus.
4. **CA21148**, Uudsetel anorgaanilistel kalkogeniididel põhinevad päikeseplatereid – rahvusvaheline koostöövõrgustik teadus- ja arendustöö läbiviimiseks.
5. **MOB3PRT17**, Jätkusuutlikud kalkogeniididel põhinevad õhukesed kiled päikeseenergiatehnoloogiale.
6. **PRG2676**, Poolläbipaistvad anorgaanilistel õhukestel kiledel põhinevad päikeseelemendid akendele ja siseruumides kasutamiseks.
7. **101183049**, Päikeseplatereidest inspireeritud anorgaanilised pooljuht-tehisevärivõrgud madala energiatarbega servaseadmetele ja visuaalõppeks.

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