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A Review on Recent Trends of Sb_2Se_3 Thin Film Technology

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ABSTRACT

Antimony selenide (Sb2Se3) thin films have emerged as a promising material for energy applications due to their unique optoelectronic properties, including high absorption coefficients, a suitable bandgap (~1-1.5 eV), and a polycrystalline orthorhombic structure. The material's abundance, non-toxic nature, and compatibility with sustainable manufacturing methods have further elevated its significance in photovoltaic and optoelectronic devices. This review provides a comprehensive analysis of the material properties, focusing on structural, optical, and electrical characteristics, along with recent advancements in synthesis techniques such as chemical and physical deposition methods. The potential of Sb2Se3 thin films in solar cell applications is highlighted, where power conversion efficiencies have steadily improved through innovative device architectures and material optimization. Additionally, this review addresses key challenges, including carrier recombination and stability issues, while proposing future research directions to enhance the performance and commercial viability of Sb2Se3-based devices. By consolidating existing knowledge, this study aims to serve as a foundation for advancing Sb2Se3 thin-film technologies.

Keywords: Energy, Solar, thin films.

I. INTRODUCTION

The escalating global demand for sustainable energy, driven by the urgent need to mitigate climate change and reduce reliance on fossil fuels, has accelerated innovation in renewable energy technologies. Photovoltaic (PV) systems, which convert sunlight directly into electricity, are central to this transition,

offering a clean and inexhaustible energy source. The International Energy Agency (IEA) projects that solar PV could account for over 33% of global electricity generation by 2050 under net-zero scenarios, underscoring its pivotal role in future energy systems[1]. Among PV technologies, thin-film solar cells have emerged as promising alternatives to traditional silicon-based cells due to their lower material consumption, flexibility, and potential for cost-effective scaling[2]. However, achieving high efficiency, sustainability, and scalability simultaneously remains a critical challenge.

The theoretical limits of PV efficiency, as defined by the Shockley-Queisser (S-Q) detailed-balance model, provide a benchmark for single-junction solar cells. This model predicts a maximum power conversion efficiency (PCE) of 33.3% for an optimal bandgap of ~1.14 eV under standard solar irradiation[3]. While this framework guides material selection, real-world efficiencies are constrained by non-ideal factors such as recombination losses, parasitic absorption, and interfacial defects[4]. For instance, leading thin-film technologies like Cu(In,Ga)Se_2 (CIGS) and CdTe have achieved laboratory efficiencies of 22.6% and 22.1%, respectively, but these drop to 19.2% and 18.6% at the module level due to scaling-related losses such as resistive interconnections and non-uniform film growth[5, 6]. Such performance gaps highlight the need for improved material quality and manufacturing processes. Beyond efficiency limitations, resource scarcity and environmental concerns hinder the large-scale deployment of CIGS and CdTe. Indium and gallium, critical components of CIGS, are scarce elements with limited global reserves; indium, for example, has an estimated terrestrial abundance of just 0.1 ppm, raising concerns about long-term supply security[7]. Additionally, cadmium, a toxic heavy metal in CdTe, poses significant environmental and health risks during production and disposal, necessitating stringent regulatory controls[8]. These challenges underscore the importance of developing PV materials that are both earth-abundant and environmentally benign.

In response, researchers have turned to alternative chalcogenides, such as Cu_2SnS_3, $CuSbS_2$, $Cu_2ZnSnSe_4$, and Sb_2Se_3, which leverage low-cost, nontoxic elements[9-11]. Antimony selenide (Sb_2Se_3) has garnered particular interest due to its optimal bandgap (~1.2 eV), high absorption coefficient (>10^5 cm^{-1} at visible wavelengths), and intrinsic stability[12, 13]. As a binary compound in the V_2-VI_3 family, Sb_2Se_3 crystallizes in a unique one-dimensional (1D) ribbon-like structure, where $(Sb_4Se_6)_\infty$ ribbons stack via van der Waals interactions. This anisotropic structure promotes directional charge transport along the ribbon axis while mitigating recombination at grain boundaries, a feature advantageous for PV applications[14, 15]. Furthermore, Sb_2Se_3's constituent elements—antimony and selenium—are more abundant than indium and gallium, with antimony reserves estimated at 2 million metric tons globally, ensuring better scalability[7].

Recent advances in Sb_2Se_3 solar cells have demonstrated remarkable progress, with efficiencies rising from below 5% to over 10% in the past decade[16]. Key breakthroughs include the development of vapor transport deposition (VTD) and rapid thermal evaporation (RTE) techniques, which enable precise control over film stoichiometry and crystallographic orientation[17]. However, several challenges persist. Defect management remains critical, as intrinsic vacancies (e.g., V_{e}) and antisite defects (e.g., Sb_{e}) can introduce deep-level traps that degrade carrier lifetime[18]. Additionally, optimizing the heterojunction interface—particularly band alignment between Sb_2Se_3 and charge-transport layers like CdS or TiO_2—is essential to minimize interface recombination and voltage losses[19]. The open-circuit voltage (VOC) deficit, defined as the discrepancy between the theoretical VOC (based on bandgap) and the measured value, remains a key performance bottleneck, with current deficits exceeding 400 mV in state-of-the-art devices[20]. Long-term stability under

thermal and humidity stress also requires improvement to meet industry standards for outdoor deployment[21].

This review comprehensively examines recent advancements in Sb_2Se_3 thin-film solar cells, focusing on synthesis methods (e.g., close-spaced sublimation, solution processing), structural and optoelectronic characterization, and device engineering strategies. We also discuss emerging approaches to address defects, enhance light harvesting, and improve interfacial properties. By overcoming these challenges, Sb_2Se_3 could emerge as a cornerstone of next-generation PV technologies, combining sustainability, efficiency, and scalability to meet global energy demands.

II. STRUCTURAL PROPERTIES

Antimony selenide (Sb_2Se_3) is gaining considerable attention due to its fascinating structural and optical characteristics. It belongs to the A_2B_3 semiconductor family, where 'A' usually denotes antimony (Sb) or bismuth (Bi), and 'B' represents chalcogens like sulfur (S) or selenium (Se)[22]. Crystallographically, Sb_2Se_3 features an orthorhombic structure, commonly described by either the Pbnm or Pnma space group, which varies based on the lattice axis orientation[23, 24]. This difference in structural description can significantly impact the material's physical attributes, such as its electronic and optical responses. Investigations have specified the lattice parameters for the Pbnm space group as a=11.62 Å, b=11.77 Å, and c=3.962 Å. In contrast, the Pnma space group parameters are a=11.7938 Å, b=3.9858 Å, and c=11.6478 Å[24]. These subtle differences in lattice dimensions underscore the complex nature of its crystal structure and its sensitivity to various synthesis methods. The atomic arrangement within this lattice consists of one-dimensional $(Sb_4Se_6)n$ chains running parallel to the c-axis. These chains are separated by inter-chain distances of approximately 2.98 Å, with interlayer spacing governed by Sb-Se bonding at about 3.46 Å (Luo et al., 2023). This quasi-one-dimensional structure leads to pronounced anisotropy in electronic and photonic properties, notably enabling efficient charge transport along the chain direction but presenting significant mobility limitations perpendicular to it[25, 26].

Furthermore, within this crystalline framework, antimony and selenium atoms occupy distinct, non-equivalent sites. Antimony atoms typically exhibit six-fold coordination, resulting in a distorted octahedral geometry. Selenium atoms, on the other hand, are generally found in seven-fold coordination, forming a tetragonal pyramidal structure[27]. This unique coordination environment creates an intricate network of polyhedra linked through selenium atoms, which bolsters the structural integrity and functional potential of Sb_2Se_3 in electronic devices[28]. Grasping these coordination details is vital for tailoring the material's properties for targeted applications, especially in photovoltaics and photodetection.

The anisotropic nature of Sb_2Se_3 extends beyond its structural features to its electronic behavior. The material exhibits markedly higher charge mobility along the c-axis compared to directions perpendicular to it. This pronounced anisotropy creates difficulties for conventional measurement techniques, like the Hall effect[29, 30]. Consequently, there is a need to develop innovative experimental methods capable of thoroughly characterizing the wide range of electrical properties inherent to Sb_2Se_3. Recent exploratory work suggests that applying strain or external electric fields can modify the electronic properties of Sb_2Se_3. This offers potential for enhancing its application in optoelectronic devices[31]. Such modifications can affect the bandgap energy and optimize carrier separation and transfer processes, thereby improving performance metrics in areas like photovoltaics, where Sb_2Se_3 has shown significant promise [32]

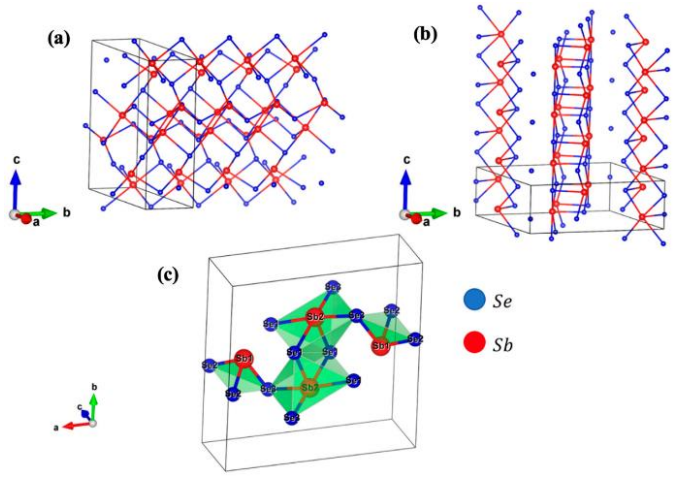

Figure. Sb_2Se_3 crystal structure that refers to (**a**) *Pnma* and (**b**) *Pbnm* space group expanded along the ribbon direction. (**c**) the non-equivalent positions of Sb and Se atoms are presented considering the *Pbnm* space group, bonds are depicted only between short- and medium- distance atoms. All figures are made with VESTA software 3.5.8[33].

III.OPTICAL PROPERTIES

Within the A_2B_3 chalcogenide family, Sb_2Se_3 has become notable as a prospective photovoltaic absorber material. This recognition is primarily driven by its optoelectronic characteristics, which make it suitable for next-generation solar cell applications. Performance analyses suggest that Sb_2Se_3, with optimized energy band structures, could potentially compete with established thin-film technologies like CdTe and $Cu(In,Ga)Se_2$, as indicated by the Spectroscopic Limited Maximum Efficiency (SLME) model—a refinement of the classic Shockley–Queisser limit.[30] This potential highlights the material's promise for advancing solar energy conversion and attracts significant interest from the solar research community.

A thorough evaluation of any new absorber material necessitates the precise characterization of its fundamental optical parameters, such as direct and indirect band gaps, the complex refractive index, and dielectric constants[34]. However, reported values for these optical constants in Sb_2Se_3 show considerable variation across different studies. This discrepancy mainly arises from differences in deposition methods and the resulting characteristics of the films[35]. For instance, research by Kumar et al. reports effective optical absorption coefficients for Sb_2Se_3 exceeding $10^5 cm^{-1}$, whereas refractive indices tend to fluctuate based on the specific film deposition techniques employed.[35] Improvements in the optical properties of Sb_2Se_3 films have been noted following post-deposition annealing. Studies show that annealing at 200°C can yield direct and indirect band gaps of approximately 1.54 eV and 1.1 eV, respectively.[36] These findings are corroborated by various studies using different deposition techniques like sputtering, thermal evaporation, and pulsed laser deposition, all indicating that thermal treatments enhance crystalline quality and improve energy band characteristics.[35, 36]

Compared to their amorphous forms, crystalline Sb_2Se_3 films demonstrate markedly superior optical properties. This advantage is attributed to improved crystallization, which leads to enhanced carrier mobility and higher electron concentration. These factors, in turn, positively influence the refractive indices and extinction coefficients[37]. Advanced characterization methods, including spectroscopic ellipsometry and photoluminescence analysis, confirm that Sb_2Se_3 behaves as a direct-bandgap semiconductor, a crucial property for applications demanding high efficiency in solar energy absorption[37, 38]. Further research into how film stoichiometry and thickness affect the band gap emphasizes the critical influence of deposition parameters on Sb_2Se_3's optical traits. This underscores the need for precise control during fabrication to achieve optimal properties for photovoltaic uses[37, 39].

The morphology of the films significantly impacts the electronic performance of resulting solar cells. Current findings indicate that optimizing stoichiometry can result in better energy level alignment and improved compatibility at the interface

with electron transport layers. For example, recent investigations have shown that using zinc tin oxide (ZTO) as an electron transport layer can boost photovoltaic efficiency[32, 34].

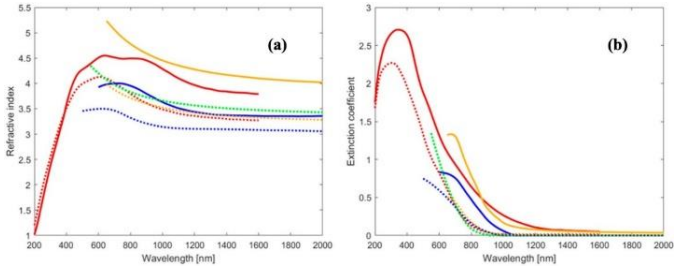

Figure. (a) Refractive index and (b) extinction coefficient from studies examining the optical properties of Sb_2Se_3 red[40], blue[41], orange[42], green[43]). Dotted lines represent amorphous films, while continuous lines correspond to crystalline films.

IV. DEFECTS IN Sb2Se3

Sb_2Se_3 semiconductor material of growing interest, contains various defects that markedly affect its structural integrity and electronic behavior, especially in photovoltaic contexts. Among the most common defect types in polycrystalline Sb_2Se_3 thin films are recombination centers located at grain boundaries. These defects critically influence carrier transport mechanisms and the overall efficiency of solar cells[44]. The most favourable orientations for photovoltaic applications involve grains aligning parallel to the ribbon directions along (h, k, l) planes where l=0. This alignment helps reduce recombination events at grain interfaces, suggesting that grains grown in these orientations exhibit somewhat passivated boundaries, characterized by (hk0) planes lacking dangling bonds, thereby minimizing scattering losse[45, 46].

The understanding of point defects within Sb_2Se_3 has advanced, particularly with insights from density functional theory (DFT) simulations. Initial DFT studies suggested a relatively simple defect landscape, primarily comprising two vacancies (VSe and VSb), two antisite defects (SbSe and SeSb), and one interstitial defect (Sei)[45]. This initial view was partly shaped by studies on semiconductors with higher structural symmetry, such as GaAs and CdTe[47]. However, Sb_2Se_3's quasi-one-dimensional structure, unlike these higher symmetry materials, features significant non-equivalent atomic sites. These sites critically impact both the ionization levels and formation energies of defects, leading to a more complex defect scenario than first assumed[45, 47]. More recent theoretical work has uncovered as many as five distinct vacancy types and five different antisite defects, pointing towards a substantially richer defect chemistry than previously recognized[45, 48].

Regarding defect formation energies, not all defects might substantially alter the electronic properties of Sb_2Se_3. For example, although selenium vacancies (VSe) are often linked to detrimental effects, acting as deep donor defects that diminish the free hole concentration, their high formation enthalpy makes direct comparisons with antimony vacancies (VSb) – characterized as either deep or shallow acceptors – complex[45, 49, 50]. Current research points to a more sophisticated understanding of how VSe impacts solar cell performance deficiencies, complicating efforts to optimize device designs[48, 51, 52]. The intricate nature of defect states in Sb_2Se_3 highlights the potential for significant enhancements through customized growth strategies that manage defect types by carefully adjusting stoichiometry during deposition. Specifically, manipulating the Sb/Se ratio during synthesis has been shown to produce notably different electronic properties. Selenium-rich conditions typically lead to a predominance of shallow acceptor defects, whereas antimony-rich conditions tend to promote the formation of deep donor defects[53, 54].

Recent studies emphasize the crucial role of defect engineering in boosting the performance of Sb_2Se_3-based solar cells. By adjusting growth parameters, such as temperature and the composition of the surrounding atmosphere, researchers can influence defect formation, aiming to either suppress undesirable states or encourage beneficial ones[48, 55,

56]. This approach offers a pathway to improved efficiency by enhancing carrier mobility and minimizing recombination losses. For instance, one study showed that precise control over the growth environment could improve the crystalline quality and lower the defect density in Sb_2Se_3 films, leading to better optoelectronic performance for solar energy conversion[52, 56].

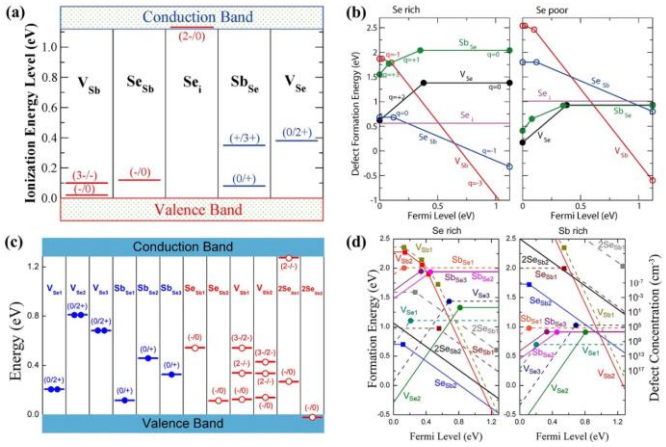

Figure (a, c) Energy levels of intrinsic point defects at various atomic sites within the bandgap of Sb_2Se_3. (b, d) Formation energies and equilibrium concentrations of intrinsic defects in Sb_2Se_3 as functions of the Fermi level under selenium-rich and selenium-poor (antimony-rich) conditions. *[Wang, Yazi, Seunghwan Ji, and Byungha Shin. "Interface engineering of antimony selenide solar cells: A review on the optimization of energy band alignments." Journal of Physics: Energy 4.4 (2022): 044002.]*

V. SURFACE MORPHOLOGY

The surface topography of Antimony Selenide (Sb_2Se_3) thin films significantly dictates their effectiveness in photovoltaic devices. This is strongly linked to the material's unique one-dimensional (1D) structure, which comprises parallel-stacked ribbons. This distinct arrangement leads to fewer dangling bonds at grain boundaries (GBs) compared to conventional three-dimensional (3D) semiconductors like silicon (Si) and gallium arsenide (GaAs)[57]. The consequent reduction in defect density at these interfaces plays a crucial role in mitigating recombination losses, which in turn boosts the photovoltaic performance of Sb_2Se_3 thin films[58].

Field-emission scanning electron microscopy (FESEM) studies show that Sb_2Se_3 thin films grown around 25 °C display varied surface morphologies influenced by deposition potentials between -0.4 V and -0.6 V. These films typically measure between 1.05 µm and 1.17 µm in thickness. The grain size and surface uniformity are observed to depend significantly on the applied potential. While higher deposition potentials tend to yield larger grains and rougher surfaces—potentially improving light trapping—they might also introduce more recombination sites. This presents a balance that must be managed between optimizing surface texture for light absorption and minimizing efficiency losses due to recombination[59, 60].

Furthermore, specific crystal planes of Sb_2Se_3, including (100), (010), (110), and (120), possess relatively low surface energy, resulting in inert and stable surfaces. First-principles simulations suggest that when Sb_2Se_3 ribbons align along the c-axis, these low-energy surfaces effectively terminate the grain boundaries. This configuration minimizes the formation of defect states that could otherwise facilitate recombination processes[57, 60]. Achieving this preferred orientation is key to optimizing charge transport, which is vital for enhancing the overall efficiency of Sb_2Se_3-based solar cells. Optimizing the efficiency of Sb_2Se_3 thin films for photovoltaic use requires careful and rigorous control over deposition conditions. Parameters such as deposition potential and substrate temperature are critical as they heavily influence surface uniformity and the density of defects. By precisely managing these factors during fabrication, the quality of the films can be improved, leading to enhanced photovoltaic performance [61, 62].

Recent progress in deposition techniques, like vapor transport deposition (VTD), has enabled the production of high-quality Sb_2Se_3 thin films featuring desirable surface morphologies. These advanced methods promote the formation of compact and well-

oriented grain structures, which are essential for efficient carrier transport [63, 64]. Additionally, adjusting the chemical makeup of precursor materials and introducing dopants have proven effective in refining surface characteristics and thereby improving device performance [65, 66].

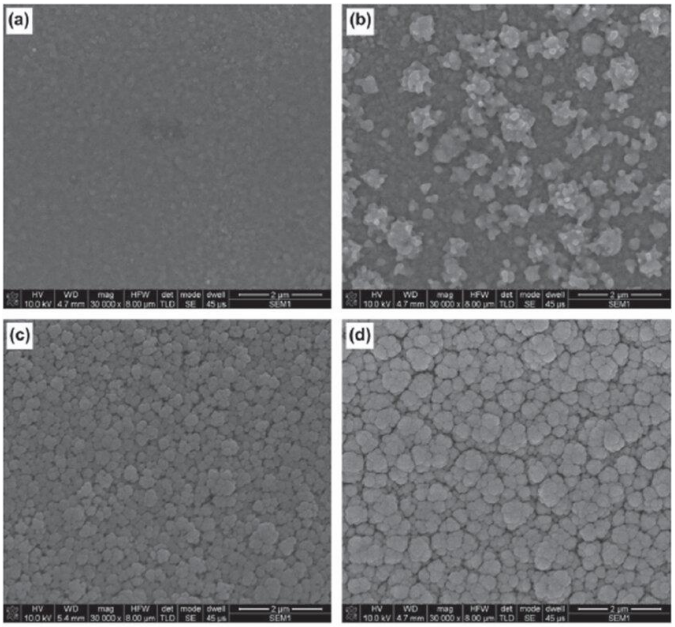

Figure The surface characteristics of antimony selenide thin films, formed at a temperature of 25 °C, exhibit variations under different deposition potentials: (a) -0.4 V, (b) -0.5 V, (c) -0.55 V, and (d) -0.6 V. The resulting film thicknesses range between 1.05 μm and 1.17 μm.[67]

VI. DEPOSITION TECHNIQUES

Developing Sb_2Se_3 thin films with low defect densities is essential for reducing the recombination of light-generated electron-hole pairs and enhancing the performance of photovoltaic devices. This factor is especially critical when depositing the Sb2Se3 absorber layer onto various electron transport layer (ETL) materials, such as CdS, ZnCdS, ZnO, TiO_2, ZnS, Zn(S,O), MgZnO, and ZnSe1. The pseudo-one-dimensional (1D) nature of Sb_2Se_3films promotes efficient charge transport along the ribbon structures, thereby minimizing recombination losses. Consequently, deposition techniques must accommodate the anisotropic growth characteristics of Sb_2Se_3 to ensure appropriate crystallization and ribbon alignment relative to the charge transport direction. Recent progress in fabricating antimony selenide (Sb_2Se_3) thin films has involved exploring both physical and chemical deposition methods. These advancements have culminated in devices achieving power conversion efficiencies (PCE) greater than 10%, positioning Sb_2Se_3 as a viable contender in the photovoltaic field (Duan et al., 2022). Within physical deposition approaches, electron-beam gun (EBG) deposition has become significant due to its high-vacuum operation, which allows for precise control over film growth conditions[68].

In a commonly employed fabrication route, Sb_2Se_3 thin films are synthesized using a two-stage process. First, a metallic antimony precursor layer is deposited via radio frequency (RF) magnetron sputtering. High-purity antimony targets are utilized for this step, and the deposition occurs onto Mo-coated soda-lime glass substrates. Before sputtering, these substrates undergo a thorough ultrasonic cleaning procedure using detergent, acetone, isopropanol, and ethanol, each for ten minutes, to ensure optimal surface cleanliness and adhesion for the subsequent thin film[69].

Following substrate preparation, the deposition chamber is evacuated to a base pressure lower than 7.0×10^{-4} Pa. High-purity argon gas (> 99.999%) is then introduced at a controlled rate of 40 standard cubic centimeters per minute (sccm). By maintaining a deposition pressure of 0.5 Pa and applying a constant RF power of 30 W, a stable deposition rate of roughly 10 nm/min is achieved[70]. The final thickness of the antimony film can be adjusted by controlling the sputtering duration, typically varying between 30 and 90 minutes in 15-minute steps, enabling the creation of films tailored for specific device requirements[39].

A crucial subsequent step involves a post-selenization heat treatment to ensure the proper crystallinity and stoichiometry of the final Sb_2Se_3films. In this process, the previously deposited antimony film is placed in a dual-chamber vacuum tubular furnace along with high-purity selenium powder (99.999%). The furnace

chambers are evacuated and subsequently purged with argon gas to establish a working pressure of approximately 5×10^4 Pa. This controlled atmosphere provides sufficient selenium vapor pressure, essential for synthesizing stoichiometric Sb_2Se_3 and minimizing selenium vacancies[39]. The system is then heated to 400 °C using a ramp rate of 20 °C/min, held at this temperature for 15 minutes, and finally allowed to cool naturally to room temperature. This thermal process facilitates the conversion of the amorphous antimony layer into crystalline Sb_2Se_3[68].

After the Sb_2Se_3 absorber layer is formed, a cadmium sulfide (CdS) buffer layer is typically deposited using the chemical bath deposition (CBD) technique. The aqueous solution for CBD contains precursors like cadmium sulfate ($CdSO_4$), thiourea, and ammonium hydroxide (NH_4OH). Specifically, a mixture comprising 0.015 M $CdSO_4$ and 0.75 M thiourea is prepared, with NH_4OH added, all dissolved in deionized water. The substrates with the Sb2Se3layer are immersed in this solution, which is maintained at 80 °C and continuously stirred for 9 minutes. Following deposition, the substrates are rinsed with deionized water and dried thoroughly before proceeding to the next fabrication stage[71].

To improve the energy band alignment and encourage elemental interdiffusion at the Sb_2Se_3/CdS heterojunction, a brief annealing step is performed at 300 °C for 5 minutes under an argon atmosphere. This treatment enhances the interfacial properties between the absorber and buffer layers[39]. The final layer deposition involves creating an indium tin oxide (ITO) window layer using direct current (DC) magnetron sputtering. This is conducted at a power of 60 W and a pressure of 0.4 Pa, with controlled argon and oxygen gas flow rates of 30 sccm[72]. Once the ITO deposition is complete, the device surface is typically sectioned into individual cells, often measuring 0.15 cm^2. As the final step, silver (Ag) electrodes are applied onto the ITO surface via thermal evaporation. This establishes the top metallic contacts, completing the Sb_2Se_3 thin-film solar cell fabrication, which results in a layered structure commonly configured as Mo/ Sb_2Se_3/CdS/ITO/Ag[39].

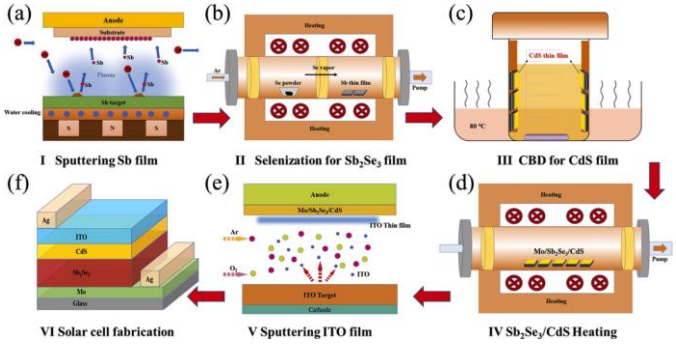

Figure A schematic representation of the fabrication process for the Sb_2Se_3 thin-film solar cell with a substrate structure is illustrated as follows: (a) Deposition of the Sb precursor thin film using RF magnetron sputtering, (b) Formation of Sb_2Se_3 thin film through post-selenization heat treatment, (c) Application of the CdS buffer layer via the chemical bath deposition (CBD) method, (d) Post-annealing of the Sb_2Se_3/CdS heterojunction, (e) Deposition of the ITO layer using magnetron sputtering, and (f) Final schematic layout of the Sb_2Se_3 thin-film solar cell[73].

A. Electron-Beam Gun (EBG) Deposition

The use of electron beam (e-beam) deposition for creating antimony selenide (Sb_2Se_3) thin films for solar cells is a method gaining recognition. This technique is valued for its capacity to produce high-quality films with well-controlled stoichiometry and morphological features. E-beam deposition employs high-energy electrons to vaporize a source material, which then condenses as a thin film onto a substrate.

A key benefit of e-beam deposition compared to techniques like thermal evaporation or sputtering lies in its ability to yield Sb_2Se_3films possessing tailored crystalline orientations and uniform compositions. Achieving favourable crystal alignment, especially along the c-axis, is vital for improving charge transport within the films, a factor that directly influences solar cell efficiency [39, 74]. E-beam deposition allows for meticulous control over the deposition rate and energy, facilitating the optimization of the film's microstructural properties,

which is crucial for the effective performance of Sb_2Se_3thin-film solar cells [39, 69].

Furthermore, several studies suggest that the electronic characteristics of films deposited via e-beam can surpass those produced by other methods. For example, Sb_2Se_3 films deposited using e-beam have demonstrated improved electrical performance, attributed to a lower density of defect states compared to films made by techniques such as sputtering or close-space sublimation[69, 75]. The unique one-dimensional crystal structure of Sb_2Se_3 inherently supports efficient photogenerated carrier transport, emphasizing the significance of controlling growth directionality through the choice of deposition technique[25, 70].

Post-deposition treatments, notably selenization, have proven effective in further enhancing the properties of e-beam deposited Sb_2Se_3 films. Such treatments aid in mitigating defects and fine-tuning stoichiometry, both critical steps for attaining higher efficiencies in solar devices[62, 76]. Consequently, combining e-beam deposition with appropriate subsequent processing steps presents promising strategies for elevating the photovoltaic performance of Sb_2Se_3-based solar cells and potentially exceeding current power conversion efficiency benchmarks[39, 69].

B. Thermal Evaporation (TE)

Employing thermal evaporation to deposit antimony selenide (Sb_2Se_3) thin films represents a viable strategy for fabricating high-efficiency solar cells. This method entails the controlled heating of antimony (Sb) and selenium (Se) source materials within a vacuum until they vaporize. The resulting vapor then condenses onto a substrate, forming a thin film. Conducting the evaporation process under vacuum conditions is crucial for minimizing contaminants and ensuring uniform film properties. Thermal evaporation offers the advantage of precise control over deposition rates, enabling the attainment of specific thicknesses and stoichiometries, which are vital for optimizing solar cell performance[77, 78].

A notable difficulty when thermally evaporating Sb_2Se_3 relates to the thermal instability of the source materials. If evaporation conditions are not meticulously regulated, this instability can lead to the formation of undesirable phases, such as antimony trioxide (Sb_2O_3). Research by Liu et al. indicates that excessive oxygen incorporation during deposition can degrade film quality, increasing surface recombination losses due to Sb_2O_3 formation[79]. This underscores the necessity for rigorous control over the deposition environment, particularly since both Sb and Se can decompose at high temperatures, potentially causing deviations from the desired stoichiometry[78].

To improve the characteristics of thermally evaporated Sb_2Se_3 films, various post-deposition treatments have been investigated. For example, work by Yao et al. shows that managing cooling temperatures and applying hydrogen sulfide treatments post-deposition can markedly enhance film crystallinity and overall electronic behavior[70]. Such post-treatment procedures can effectively heal defects within the film structure, thereby fostering better charge carrier mobility and ultimately improving device efficiency, a critical factor for solar energy applications[70] (Yao et al., 2020). Furthermore, the choice of substrate significantly influences the growth orientation of the film; selecting appropriate substrates can promote more favorable columnar growth structures, which enhance the effective active area and light absorption capabilities essential for efficient photovoltaic conversion[76].

Although alternative deposition techniques like co-evaporation and vapor transport deposition are widely used, thermal evaporation remains a consistently effective method owing to its inherent scalability and operational simplicity. Consequently, early solar cell devices fabricated using thermally evaporated Sb_2Se_3 films have achieved reported efficiencies exceeding 6.7%[61]. Ongoing advancements in deposition protocols and optimized solar cell designs continue to drive these efficiency figures upward. Enhancements in stoichiometry control and phase purity, realized

through careful management of thermal evaporation parameters, have been demonstrated to significantly boost the photovoltaic response of these films[79, 80].

C. Vapor Transport Deposition (VTD)

The technique of vapor transport deposition (VTD) for preparing antimony selenide (Sb_2Se_3) thin films has attracted interest for solar cell development, primarily because it allows for the production of high-quality, uniform films with controllable characteristics. VTD functions by heating a solid Sb_2Se_3precursor material in a vacuum environment. The generated vapor subsequently travels and condenses onto a substrate maintained at a lower temperature, where it reforms into a solid film[63]. This process, involving a solid-to-vapor-to-solid transition, is instrumental in obtaining the desired microstructural features essential for effective photovoltaic operation.

A primary benefit of VTD is its capability to facilitate the growth of Sb_2Se_3 films with accurate stoichiometry. This method offers superior control over the chemical composition and helps minimize the formation of detrimental defects, such as selenium vacancies and antimony antisites, which can negatively impact the film's electrical properties[39]. Films produced via VTD can exhibit high optical absorption coefficients, ideally exceeding $10^5 cm^{-1}$, and possess a bandgap typically in the range of 1.1 eV to 1.3 eV. These properties make them well-suited as absorber layers for efficient photovoltaic devices[81].

Research indicates that Sb_2Se_3 solar cells fabricated using VTD can potentially achieve efficiencies over 10%, attributed to improved electrical transport characteristics and reduced recombination losses. It has been reported, for example, that the open-circuit voltage (Voc) and fill factor (FF) of VTD-produced solar cells are significantly enhanced compared to devices made using alternative techniques like thermal evaporation or chemical bath deposition[39]. Champion solar cells fabricated via VTD have demonstrated efficiencies reaching 7.6%, positioning this method competitively among emerging thin-film photovoltaic technologies[63].

Furthermore, incorporating sulfur during the VTD process presents a promising avenue for modifying the electronic properties of Sb_2Se_3 films, potentially enabling the creation of gradient bandgap structures. Such structures can lead to better interfacial charge transport by minimizing energy mismatches at interfaces with adjacent layers, thereby boosting overall cell performance[82]. The addition of sulfur is particularly noteworthy as it can help address issues related to selenium deficiency, which sometimes occurs during deposition and can adversely affect film quality[82].

The careful optimization of VTD parameters, including substrate temperature and the duration of deposition, is critical in controlling the resulting film morphology and degree of crystallinity. By adjusting these parameters, it is possible to encourage preferential crystal growth orientations, which is advantageous for enhancing charge carrier mobility within the thin films[51]. Additionally, refining the interfacial architecture, often through the strategic use of buffer layers, has been shown to effectively reduce surface recombination effects, thereby maximizing the efficiency potential of Sb_2Se_3 solar cells manufactured using VTD[83].

D. Sputtering Deposition of Sb2Se3 Thin Films for Solar Cells

Paraphrased Text:

Sputtering deposition stands as a prevalent technique for producing antimony selenide (Sb_2Se_3) thin films, especially those intended for solar cell applications. This physical vapor deposition method works by bombarding a target material, usually Sb_2Se_3, with energetic ions. This bombardment dislodges atoms from the target, which then travel and deposit onto a substrate. Sputtering is primarily carried out using either direct current (DC) magnetron sputtering or pulsed magnetron sputtering. Both variations have demonstrated considerable promise for generating high-quality thin films with the controlled properties necessary for effective photovoltaic conversion[84, 85].

A significant advantage offered by sputtering is its capability to deposit films with consistent thickness across large surface areas, a critical factor for the scalable manufacturing of solar cells[85]. The technique allows for precise management of the deposited material's composition. This enables controlled doping, for instance, introducing elements like copper to boost hole concentration in Sb_2Se_3 films, thereby potentially enhancing their electrical conductivity and overall solar cell efficiency[84]. Furthermore, adjusting sputtering parameters—such as the working pressure, applied power, and distance between the target and substrate—directly affects the morphology and crystalline quality of the resulting films. Studies have shown that modifying the working pressure during deposition can improve both the crystallinity and the preferential orientation of Sb_2Se_3 thin films, factors vital for optimizing their photovoltaic characteristics[68].

The crystalline structure of films produced by sputtering is crucial for efficient energy conversion. Films exhibiting specific preferred orientations, like the (hk0) or (hk1) planes, generally show superior electronic properties that facilitate better charge transport[86]. Research confirms that optimizing the sputtering process can yield films with the desired grain alignment, leading to enhanced light absorption capacity and reduced recombination losses at interfaces. Achieving this optimized structure is particularly important due to Sb_2Se_3's quasi-one-dimensional crystal nature, which inherently supports efficient charge carrier movement along the crystal lattice[30, 86].

Additionally, post-deposition annealing treatments can markedly improve the performance characteristics of sputtered Sb_2Se_3 films. Subjecting these films to thermal processing can enhance their crystallization and promote the healing of defects, which contributes to increased efficiency in the final solar cell devices[87]. Several studies have documented significant improvements in solar cell performance following such treatments, achieving efficiencies exceeding 9%[14].

It is important to note that the sputtering method does have limitations. A key challenge involves the potential decomposition of the target material at elevated temperatures, which can alter the film's stoichiometry and introduce defects. This necessitates careful calibration and control of the deposition parameters[88]. Despite this, ongoing progress in sputtering technology, coupled with a deeper understanding of Sb_2Se_3's material properties and deposition dynamics, continues to advance the potential for achieving even higher performance solar cells using this technique.

Chemical Deposition Methods

Chemical Bath Deposition (CBD) represents a significant research avenue for producing antimony selenide (Sb_2Se_3) thin films within the photovoltaics sector, particularly for solar cell fabrication. This technique is noted for its cost-effectiveness, environmentally benign nature, and capability to yield high-quality thin films. The synthesis of Sb_2Se_3 using CBD relies on the chemical reactions between various precursors dissolved in a solution under controlled temperature conditions, facilitating the deposition of the desired semiconductor material onto different substrates. Its scalability and effectiveness in generating homogeneous thin films make CBD particularly advantageous for solar cell manufacturing. The principle behind Chemical Bath Deposition involves controlled chemical reactions within a solution, where metal ions and chalcogen source materials react and precipitate onto a substrate, typically at lower temperatures than those required for methods like thermal evaporation or sputtering. The reaction conditions are crucial; factors such as the solution's pH, temperature, and the concentration of reactants significantly impact the nucleation process, growth rate, and the crystalline quality of the resulting film. For instance, maintaining a specific pH range can optimize the solubility of antimony and

selenium precursors, promoting favorable film deposition[89, 90].

Sb_2Se_3 materials have garnered attention due to their favorable properties, including a suitable bandgap of around 1.1 eV, which effectively matches the solar spectrum for efficient light absorption[91]. Numerous studies report substantial progress in the efficiency of Sb_2Se_3-based solar cells, with recent figures surpassing 10%[84]. These improvements are partly linked to the adoption and optimization of various deposition techniques, CBD included, which enable the growth of high-quality films possessing desirable optoelectronic characteristics[39].

Comparative studies indicate that films produced via CBD can possess advantageous structural properties. These properties contribute to enhanced charge carrier mobility and reduced recombination losses, both of which are essential for boosting the power conversion efficiency (PCE) of solar cells[51]. For example, films grown under carefully optimized CBD conditions often exhibit crystalline structures conducive to effective charge transport, a critical factor for achieving high-performance solar cells[92].

Furthermore, the CBD method inherently helps in preventing the formation of detrimental phases, such as antimony trioxide (Sb_2O_3), at the critical interface between the Sb_2Se_3 absorber layer and the electron transport layer, which often impairs device performance[62]. By carefully managing the deposition microenvironment, the crystalline quality of Sb_2Se_3 films can be significantly enhanced, directly influencing the device architecture and its overall efficiency. Researchers have realized notable improvements in Sb_2Se_3 solar cells through meticulous investigation of growth parameters like temperature and precursor concentrations during the CBD process[30].

A primary challenge that persists with the CBD technique is achieving precise control over film thickness and uniformity across the substrate. These parameters are vital because variations can lead to inconsistencies in electrical properties throughout the film, negatively impacting overall device performance[93]. Nonetheless, ongoing advancements in real-time monitoring methods and chemical process control have led to better uniformity and reproducibility for Sb_2Se_3 films deposited using CBD[94].

The selection of substrate material further reinforces the utility of CBD for Sb_2Se_3 deposition. Substrates like titanium dioxide (TiO_2), for example, have shown potential in promoting improved adhesion and better electronic interfacing with the Sb_2Se_3 layer. This, in turn, can enhance the charge extraction efficiency of the solar cells [32, 95]. Such synergistic substrate effects can lead to superior photovoltaic performance, underscoring the importance of selecting optimal substrates within film deposition strategies.

Additionally, recent innovations include employing doping strategies to fine-tune the electronic properties of CBD-grown Sb_2Se_3 films. Research demonstrates that incorporating elements like copper can increase conductivity and modify the band structure, resulting in improved charge collection and enhanced overall cell performance[83, 84]. These modifications not only boost efficiency but also offer potential pathways to further decrease manufacturing costs, making the integration of Sb_2Se_3 into the solar energy market more feasible.

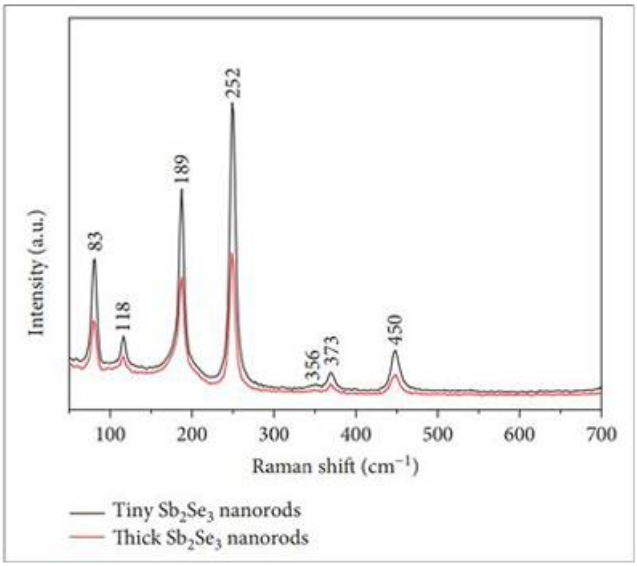

Figure Raman spectra of both tiny and thick Sb_2Se_3 samples.[96]

VII. FUTURE PROSPECTS

The future prospects of Sb_2Se_3 solar cells appear promising as the research and development in this field continues to advance rapidly. Several factors contribute to this optimism, including the material's inherent attributes, ongoing advancements in fabrication techniques, and the potential for innovative device architectures. However, there are notable challenges that need to be addressed for Sb_2Se_3 solar cells to realize their full potential in commercial applications.

Key Challenges Facing Sb_2Se_3 Solar Cells

Despite the advantageous properties of Sb_2Se_3, there are significant issues affecting the performance and scalability of solar cells based on this material:

1. **Recombination Losses**: One of the most pressing challenges is the issue of non-radiative recombination, which hinders the efficiency of energy conversion in these cells. This loss is primarily due to deep-level defects and grain boundaries in the absorber layer [56, 97]. Addressing these issues through improved doping techniques or surface treatments is crucial for future development.
2. **Doping Limitations**: Achieving effective p-type doping in Sb_2Se_3 has been challenging, which limits the charge carrier concentration needed for efficient operation [72, 98]. Current research is focusing on innovative doping methods, including the exploration of new materials that can enhance p-type conductivity while minimizing defect formation.
3. **Device Architecture Optimization**: The transition from traditional superstrate configurations to substrate configurations can lead to performance improvements by allowing better interface engineering [73, 76]. However, the need for optimized buffer layers, adequate charge transport, and reduced recombination rates adds complexity to device design and fabrication.

Strategies for Improvement

1. **Enhanced Surface Passivation**: Effective surface passivation techniques can significantly reduce recombination risks at grain boundaries. Recent studies suggest using various thin film coatings and doping methods that improve carrier lifetimes and overall device efficiency[16, 85].
2. **Control of Crystal Orientation**: Manipulating the crystal growth orientation of Sb_2Se_3films can enhance charge carrier mobility. Research into templated growth and post-deposition treatments shows promise in achieving a more directed crystal structure, which can reduce defects and improve efficiency [76, 80, 91].
3. **Innovative Buffer Layer Materials**: The use of alternative materials, such as ZnSe and In_2S_3, as buffer layers in Sb_2Se_3 solar cells can provide better alignment and enhance electron mobility, thus improving device performance[99, 100]. This shift is crucial in creating cadmium-free devices that do not compromise efficiency.
4. **Continuous Research and Development**: The ongoing exploration of hybrid fabrication techniques, such as combining different deposition methods, can result in better quality films and improved photovoltaic performance [73, 85, 101]. Each advancement contributes to refining production processes, ultimately promoting higher efficiency and better scalability.
5. **Financial and Policy Support**: There is a need for increased funding and policy support for research in renewable energy technologies. Collaboration among academic institutions, industry, and government can facilitate the development and commercialization of Sb_2Se_3 solar cells, integrating them into existing energy infrastructures[102].

While the future prospects for Sb_2Se_3 solar cells are optimistic due to their favorable attributes and advancements in technology, significant challenges related to efficiency, material properties, and device

architecture must be systematically addressed. Enhanced research efforts focused on improving doping strategies, optimizing device design, and exploring innovative fabrication methods are key to unlocking the full potential of this promising photovoltaic technology.

VIII. CONCLUSION

This review has synthesized the current understanding and recent advancements concerning antimony selenide (Sb_2Se_3) as a promising material for thin-film photovoltaic applications. Driven by its inherent advantages – including earth-abundant constituents, low toxicity, a high optical absorption coefficient, and a near-optimal direct band gap – Sb_2Se_3 presents a compelling case for sustainable, next-generation solar energy conversion. Its unique quasi-one-dimensional crystal structure, composed of $(Sb_4Se_6)n$ ribbons, significantly influences its anisotropic charge transport properties and complex defect physics, differentiating it from conventional 3D semiconductors.

Significant progress has been achieved in fabricating Sb_2Se_3 thin films using diverse techniques such as thermal evaporation, sputtering, electron-beam deposition, vapor transport deposition (VTD), and chemical bath deposition (CBD), each offering distinct advantages and challenges regarding film quality, scalability, and cost. These efforts have successfully pushed power conversion efficiencies beyond the 10% benchmark in laboratory settings, demonstrating the material's potential. However, realizing the full theoretical potential of Sb_2Se_3 requires overcoming persistent challenges. Chief among these is managing detrimental recombination losses originating from bulk defects (like VSe and VSb) and grain boundaries, achieving effective and controllable p-type doping, and optimizing the device architecture, particularly interfaces with transport layers.

Future research must continue to focus on refining deposition processes to gain precise control over stoichiometry, morphology, and, crucially, the preferred crystal orientation (e.g., (hk0) or (hk1) planes parallel to the substrate) to leverage the anisotropic charge transport inherent in its structure. Developing effective defect passivation strategies, both at surfaces/interfaces and within the bulk, remains paramount. Furthermore, exploring and optimizing alternative, potentially cadmium-free, buffer and electron transport layers (like ZnSe, In_2S_3, or ZTO) is essential for enhancing charge extraction, improving band alignment, and boosting overall device performance and environmental compatibility. Band structure engineering through controlled doping or alloying also presents opportunities to fine-tune electronic properties. Finally, rigorous investigation into the long-term stability and operational reliability of Sb_2Se_3 devices under realistic conditions is imperative for successful commercial translation.

Sb_2Se_3 has firmly established itself as a highly promising, cost-effective, and sustainable material for thin-film photovoltaics. Continued, dedicated efforts in materials processing, fundamental defect understanding, interface engineering, and device design optimization hold the key to unlocking its full potential. With sustained advancements addressing the current challenges, Sb_2Se_3-based solar cells are well-positioned to emerge as a significant and competitive technology within the expanding renewable energy landscape.

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