TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

DEVELOPMENT OF Sb_2Se_3 THIN FILM SOLAR CELLS BY VAPOR TRANSPORT DEPOSITION

Sb_2Se_3 ÕHUKESEKILELISTE PÄIKESEPATAREIDE ARENDAMINE AURTRANSPORTSADESTAMISE MEETODIL

MASTER THESIS

Laboratory for Thin Film Energy Materials

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Tallinn 2023

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Department of Materials and Environmental Technology

THESIS TASK

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Thesis topic:

DEVELOPMENT OF Sb_2Se_3 THIN FILM SOLAR CELLS BY VAPOR TRANSPORT DEPOSITION

Sb_2Se_3 ÕHUKESEKILELISTE PÄIKESEPATAREIDE ARENDAMINE AURTRANSPORTSADESTAMISE MEETODIL

Thesis main objectives:

1. Study the theoretical background on Sb_2Se_3 thin films.
2. Employ VTD deposition method for fabricating TiO_2/Sb_2Se_3 solar cells.
3. To study the impact of VTD deposition substrate temperature on Sb_2Se_3 thin films.

Thesis tasks and time schedule:

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CONTENTS:

PREFACE

I would like to express my deepest gratitude to my supervisor, Rober Krautmann, for his invaluable guidance, support, and insightful discussions throughout the course of this thesis. His expertise and knowledge, along with the guidance of Dr. Ilona Oja Acik, the head of the Laboratory for Thin Film Energy Materials, have been instrumental in shaping the direction of my research and refining my understanding of the subject matter.

I am also grateful for the assistance and valuable inputs provided by Sajeesh Vadakkedath Gopi in data collection and analysis. His expertise and attention to detail have greatly contributed to the accuracy and reliability of the results presented in this thesis.

The research for this thesis was conducted at Tallinn University of Technology within the Department of Materials and Environmental Technology. I would like to express my gratitude for the essential resources and support provided by the department, which were invaluable in carrying out this research. The majority of the thesis work took place in the Laboratory for Thin Film Energy Materials, established by Prof. Malle Krunks and headed by Dr. Ilona Oja Acik. The labs exceptional research environment and the expertise of its members played a crucial role in the successful completion of this work. I am truly thankful for the opportunity to work in such a supportive and knowledgeable research environment at Tallinn University of Technology.

I would also like to acknowledge the contributions of other individuals in the department and the lab who have aided, insightful discussions, and inspiration throughout the research process. Their contributions have significantly enhanced the quality and impact of this thesis.

In summary, this thesis focuses on the development of Sb_2Se_3 thin film solar cells using vapor transport deposition at different substrate temperatures. The research investigates the influence of deposition parameters on the structural, morphological, and optoelectronic properties of solar cells. The results demonstrate the impact of substrate temperature on the performance of the fabricated Sb2Se3 thin film solar cells, with higher temperatures leading to improved efficiency.

Keywords: Sb_2Se_3 solar cells, Vapor Transport Deposition, Ultrasonic Spray Pyrolysis, Thin film solar cells, Master Thesis

List of abbreviations and symbols

PV	Photovoltaics
c-Si	Crystalline silicon
CdTe	Cadmium telluride
CIGS	Cadmium indium gallium selenide
CIS	Cadmium indium diselenide
Sb_2Se_3	Antimony Triselenide
CSS	Close-spaced sublimation
VTD	Vapour transport deposition
GBs	Grain boundaries
RTE	Rapid thermal evaporation
PCE	Photoconversion efficiency
CBD	Chemical bath deposition
USP	Ultrasonic spray pyrolysis
Eg	Band gap energy
TCO	Transparent conductive oxide
SE	Secondary electrons
SEM	Scanning electron microscopy
XRD	X-ray diffraction
EQE	External quantum efficiency
FF	Fill Factor
J_{SC}	Short circuit current density
V_{OC}	Open circuit voltage

1. Introduction

The increasing global demand for energy and the growing concerns over climate change have intensified the search for clean, renewable energy sources. Solar energy, harnessed through photovoltaic (PV) technology, plays a pivotal role in addressing these challenges. Photovoltaics convert sunlight into electricity, contributing to a more sustainable energy future. To meet the Paris Agreement's target of limiting global temperature rise to below 2 °C, the share of renewable energy in electricity generation must reach 86% by 2050 [1][2]. At present, solar PV represents around 2% of total world electricity generation, with a cumulative capacity of approximately 400 GW [3]. To achieve the goals set in the Paris Agreement, the installed solar PV capacity must exceed 8,500 GW by 2050 [2].

Crystalline silicon (c-Si) solar panels currently dominate the global PV market, representing approximately 90% of solar installations [4]. However, the increasing global energy demand and the need for innovative applications have sparked the search for new PV technologies. Thin film PV based on Sb-chalcogenides has emerged as a promising alternative due to its potential to revolutionize the solar industry.

Thin film PV offers several advantages, including lower manufacturing costs compared to c-Si panels and the ability to be used in innovative applications such as flexible solar cells, building-integrated PV, and internet-of-things (IoT) devices. As the concentration of Si module manufacturing in China raises geopolitical concerns, the development of alternative technologies within Europe has gained significance.

Moreover, sustainability is a key factor driving the adoption of thin film PV. These technologies are made of environmentally friendly materials that are abundant and non-toxic, aligning with the goals outlined in the European Union's sustainability initiatives [5].

By exploring thin film PV based on Sb-chalcogenides, we can address the challenges of cost reduction, expand the range of PV applications, promote regional manufacturing capabilities, and contribute to a more sustainable energy future.

Sb_2Se_3 is an emerging thin-film PV absorber material that has attracted significant attention in recent years due to its excellent optoelectronic properties and compatibility with established thin film deposition techniques [6]. Vapor transport deposition (VTD) is a particularly suitable method for depositing Sb_2Se_3 thin films, as it can produce large-grained films with preferred orientation and low grain boundary density [7]

The primary focus of this thesis is the development of Sb_2Se_3 thin film solar cells by vapor transport deposition. In the following chapters, a comprehensive theoretical background of Sb_2Se_3 solar cells, the physics of solar cells, deposition methods, and characterization techniques will be provided. The experimental section will detail the fabrication of Sb_2Se_3 solar cells at different temperatures with VTD deposition technique. Material characterization methods, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), will be employed to investigate the properties of the Sb_2Se_3 thin films and solar cells. Finally, the performance of the fabricated Sb_2Se_3 solar cells will be evaluated through current-voltage (J-V) characteristic measurements and external quantum efficiency (EQE) analysis.

Vapor transport deposition (VTD) is a simple, low-cost, and rapid technique used for fabricating Sb_2Se_3 thin film solar cells. This method allows for improved control over film thickness and composition, making it highly advantageous. Additionally, it enables the production of compact films with large grains, favorable grain orientation, and low grain boundary (GB) density [7]. These characteristics play a crucial role in achieving high-performance solar cells by facilitating enhanced charge transport and minimizing recombination losses.

The properties and performance of the resulting Sb_2Se_3 films are influenced by various factors, including evaporation temperature, inert gas pressure, distance between the source and substrate, and substrate temperature [8]. In this thesis, we specifically focused on optimizing the source and substrate temperatures in the VTD process. Previously optimized source temperature of 500 $^{\circ}$C was used, while Sb_2Se_3 thin films were deposited at different source temperatures ranging from 400 to 460 °C. The impact of the source temperature on the structural properties of Sb_2Se_3 and the device properties of complete Sb_2Se_3 PV devices was thoroughly investigated.

By systematically studying the deposition and characterization processes of Sb_2Se_3 solar cells, this thesis aims to contribute to the development of efficient and cost-effective thin-film solar cell technologies. The results and findings presented in this work will shed light on the optimization of device performance and pave the way for further advancements in the field of Sb_2Se_3 PV devices.

2. Theoretical Background

2.1. Fascinating Properties of Antimony selenide (Sb_2Se_3)

Antimony selenide (Sb_2Se_3) has emerged as a promising thin film PV absorber material. It possesses attractive properties, including an optical bandgap energy (Eg) ranging from 1.1 to 1.3 eV and a high absorption coefficient exceeding 105 cm-1 [9]. Similar to CdTe, Sb_2Se_3 is naturally a p-type material [10]. Additionally, Sb and Se, the constituents of Sb_2Se_3, are relatively abundant and environmentally friendly [9].
Sb_2Se_3 is a non-toxic binary compound with a well-defined composition and a single phase [9] [11]. It exhibits a relatively low melting point of 608 °C [12] [13] and a high vapor pressure of approximately 1200 Pa at 550 °C [13] [14]. These characteristics make Sb_2Se_3 compatible with low-temperature vacuum-based deposition techniques that are already established for CdTe photovoltaics [14].

Another exciting feature of Sb_2Se_3 lies in its one-dimensional (1D) crystal structure [13]. Sb_2Se_3 crystals are composed of $(Sb_4Se_6)_n$ ribbon-like units stacking along the c-axis, in the [001] crystal direction, resulting in highly anisotropic properties [17]. While strong covalent bonds form between Sb and Se in the [001] direction, neighboring units only bond through weak van der Waals forces in the [100] and [010] directions [13]. Interestingly, van der Waals interactions prevent the formation of dangling bonds at the grain boundaries (GBs), which are the main cause of non-radiative recombination losses that often limit the performance of polycrystalline CdTe and CIGS [18].

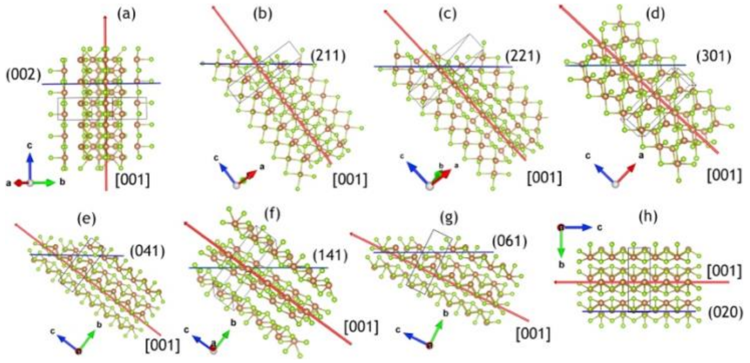

Figure 1: Different orientations of Sb_2Se_3 grains [43]

2.2. Sb_2Se_3 PV device architecture

Thin film solar cells are created by depositing one or more layers of semiconductor materials onto the substrate. Sb_2Se_3 solar cells can be fabricated in two different device architectures: superstrate and substrate. In the superstrate configuration, the device layers are stacked on a glass substrate that is coated with a transparent conductive oxide (TCO). Common TCO materials include fluorine-doped tin oxide (FTO) and indium-doped tin oxide (ITO) [15]. In this configuration, a buffer layer is first deposited on the FTO, followed by the Sb_2Se_3 absorber layer. The buffer layer, also known as the electron transport layer (ETL), forms a p-n junction with the Sb_2Se_3 layer, which is essential for the separation of the electron-hole pair excited in the absorber[16]. The buffer layers are typically thin (up to 100 nm) and have a wide bandgap (Eg), allowing most of the incident light to pass through into the absorber layer. Common materials used for the buffer layer in Sb_2Se_3 PV devices include cadmium sulfide (CdS) and titanium dioxide (TiO_2). The superstrate cells are completed by depositing metal back contacts, usually made of gold (Au), on top of the Sb_2Se_3 layer.

In the substrate devices, the layer deposition is done in reverse order. An opaque molybdenum (Mo) layer, which serves as the back contact, acts as the substrate layer onto which subsequent layers are stacked. The Sb_2Se_3 thin films are deposited directly on the Mo layer, followed by the deposition of the buffer layer and TCO. Aluminium-doped zinc oxide (AZO) is the typical TCO material used in substrate PV devices, acting as the front contact [15].

2.3. Physical deposition methods for fabricating Sb_2Se_3 thin films

Favorable material properties of Sb_2Se_3 have led researchers to explore various physical deposition methods, like vapor transport deposition (VTD), close-spaced sublimation (CSS), sputtering and sputtering are among the most commonly employed physical methods for depositing Sb_2Se_3 thin film. Each method has its advantages and challenges, with factors such as film uniformity, grain size, and preferred crystal orientation influencing the final device performance [17].

Vapor transport deposition (VTD) is a deposition method that offers precise control over film thickness and stoichiometry, which are critical for achieving high-quality absorber layers. One advantage of VTD is its ability to deposit large-area films, making it suitable for scaling up production. However, it should be noted that VTD may require longer growth times compared to other deposition techniques, potentially impacting the process throughput and overall cost [18].

One of the key benefits of VTD is its capability to independently control the source and substrate temperatures. By adjusting these parameters, it is possible to optimize the deposition conditions and achieve desired film properties. Additionally, the use of a larger distance between the source powder and substrate, along with the incorporation of a carrier gas for vapor flux transportation, allows for slower deposition rates. This slower rate facilitates better control of crystal growth and ensures more even mixing of the vapor flux, which consists of Sb_2Se_3, Sb, and Se vapors. These factors contribute to improved control over the deposition process and the resulting film properties.

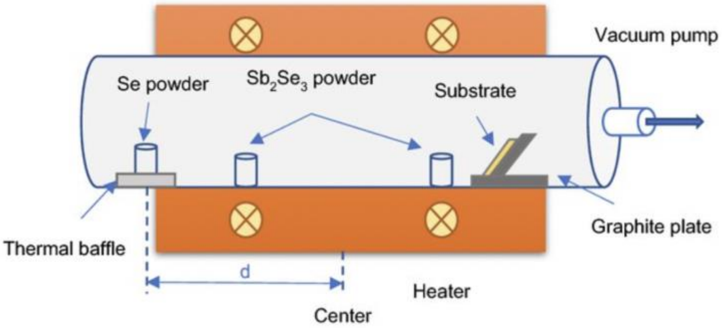

Figure 2: Schematics of the VTD system. [19]

Close-spaced sublimation (CSS) is a promising technique that also offers independent control of source and substrate temperature, allowing for precise tuning of the deposition process [20]. In CSS, the distance between the source and substrate is small, at around 1 cm, resulting in larger deposition rates compared to the vapor transport deposition (VTD) process. The small enclosed hot-walled reactor chamber in CSS provides favorable conditions for even mixing of the vapor flux, promoting uniform and stoichiometric film growth [21]. However, one disadvantage of CSS is the close proximity between the source and substrate, which may lead to the re-evaporation of selenium from the already formed thin film, this is because selenium has a higher vapor pressure than antimony, the main component of Sb_2Se_3 [21].

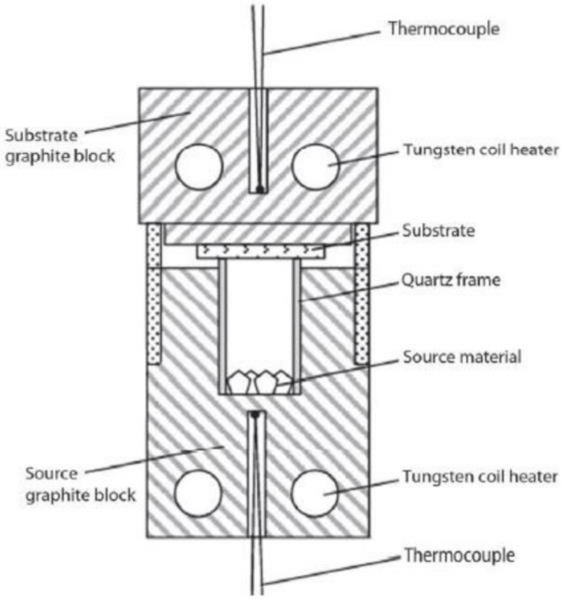

Figure 3: Schematic of the CSS system. [21]

Sputtering is a widely used deposition technique for fabricating Sb_2Se_3 thin films. It offers precise control over film thickness, uniformity, and stoichiometry, making it a versatile and scalable process. However, sputtering requires optimization of various parameters, including gas pressure, target-substrate distance, and sputtering power, to achieve the desired film properties and device performance. One important aspect of sputtering is the two-stage process involved, where the first stage involves depositing a pure Sb film, followed by the selenization of Sb into Sb_2Se_3.[22] This necessitates careful optimization of processing conditions. It is worth noting that sputtering is generally slower and more energy-intensive compared to VTD and CSS deposition methods.

2.4. Recent progress of Sb_2Se_3 Photovoltaic Devices

The progress in Sb_2Se_3 solar cells has been rapid, with power conversion efficiencies (PCEs) exceeding 10% in the last ten years [23]. This rapid progress demonstrates the potential of Sb_2Se_3 as an emerging photovoltaic absorber material. According to the Shockley-Queisser limit, the maximum theoretical efficiency Sb_2Se_3 PV devices can reach is >30% [24].

Early studies on photovoltaics mainly focused on understanding the fundamental properties and deposition techniques of this promising material. The first report on Sb_2Se_3 solar cells was published in 2012, demonstrating a power conversion efficiency (PCE) of 1.9% [25]. In the following years, researchers have been focusing on optimizing the processing conditions, exploring various device structures, and adopting strategies for effective interface engineering to enhance the performance of Sb_2Se_3 solar cells.

The first significant breakthrough in Sb_2Se_3solar cell efficiency was achieved in 2015, when researchers reported a PCE of 4.9% using a superstrate configuration and a CBD-CdS window layer. This milestone demonstrated that Sb_2Se_3-based solar cells had the potential for high efficiency and encouraged further research in the field. In recent years, the development of Sb_2Se_3 solar cells has been marked by various milestones, including the discovery of Sb_2Se_3's favorable one-dimensional crystal structure and its impact on grain boundary properties, which can minimize non-radiative recombination losses [17]. Researchers have also explored the impact of various window layer materials on device performance, such as TiO2 and ZnO, to further optimize the solar cell structure [26]. By 2018, the record efficiency of Sb_2Se_3 solar cells had reached 7.6% using a modified CSS deposition method and a ZnO window layer [14]. Further improvements in device architecture and interface engineering have contributed to the steady increase in device efficiency, with a record PCE of 9.2% reported in 2021. Recently, a novel method of injection vapor deposition (IVD) has been employed, pushing the efficiency beyond 10% [23].

In the context of this thesis on the development of Sb_2Se_3 thin film solar cells by vapor transport deposition (VTD) onto a TiO2 buffer layer, several works in the literature serve as valuable references and sources of inspiration. Wen et al. [14] laid the groundwork for understanding the potential of VTD for depositing Sb_2Se_3 thin films by reporting the fabrication of Sb_2Se_3 thin film solar cells using VTD, achieving a power conversion efficiency (PCE) of 7.6%. Building upon this foundation, Li and Tang [28] presented a super-flexible Sb_2Se_3 solar cell fabricated using VTD, which highlights the potential of Sb_2Se_3 for flexible photovoltaic applications and serves as an additional motivation for this thesis. In addition to the potential of VTD for depositing Sb_2Se_3 thin films, optimizing the solar cell structure is essential for achieving high efficiencies. Li et al. [29] demonstrated this by achieving a 7.5% efficient n-i-p Sb_2Se_3 solar cell with copper thiocyanate (CuSCN) as a hole-transport layer. Similarly, Tao et al. [30] reported a highly efficient Sb_2Se_3 thin film solar cell with a solution-processed tin oxide (SnO_2) interfacial layer, achieving an efficiency of 9.5%.

Their work can serve as a benchmark for the performance of solar cells fabricated in this thesis. Understanding the impact of crystal growth promotion and defect healing in Sb_2Se_3 solar cells is also crucial. Liang et al. [27] demonstrated this by optimizing the VTD process to minimize the open-circuit voltage deficit, which will be crucial in achieving high efficiencies in the solar cells fabricated in this thesis. Finally, Hobson et al. [31] contributed to the exploration of novel solar cell configurations by fabricating isotype heterojunction solar cells using n-type Sb_2Se_3 thin films. Their study offers insights into potential alternative solar cell structures, which may be considered for future research.

These studies illustrate the growing interest in Sb_2Se_3 thin film solar cells and the ongoing advancements in VTD techniques for their fabrication. By building upon this body of research, this thesis aims to contribute to the development of Sb_2Se_3 solar cells with improved performance and further the understanding of the VTD process for Sb_2Se_3 deposition onto TiO2 buffer layers.

The studies mentioned above are crucial for understanding the current state of the art in Sb_2Se_3 thin film solar cells and their fabrication using VTD. As the field of Sb_2Se_3 photovoltaics continues to evolve, new insights into the growth and optimization of Sb_2Se_3 thin films using VTD will be essential for realizing the full potential of this promising absorber material. By leveraging the knowledge gained from these studies, this thesis will explore the effects of different temperatures during the VTD process on the absorber layer deposited onto a TiO_2 buffer layer, aiming to contribute to the development of high-performance Sb_2Se_3 thin film solar cells.

2.5. Physics of PV Devices

Solar cells, also known as photovoltaic (PV) cells, are devices that convert sunlight directly into electrical energy through the photovoltaic effect [32]. The physics of solar cells involves understanding the interaction of photons with semiconductor materials, the generation and separation of charge carriers, and the collection of these carriers at the contacts to generate electrical power.

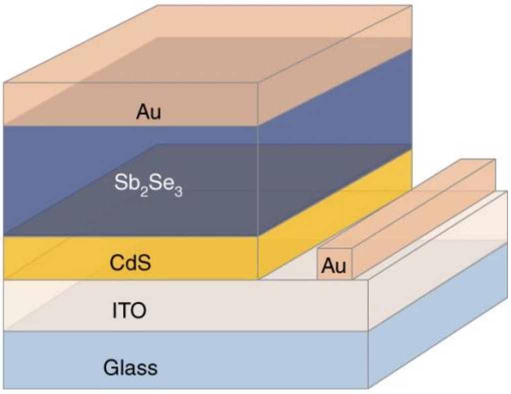

Figure 4. Schematic of a Sb_2Se_3 thin film solar cell with 7.6% efficiency [14]

2.5.1. Formation of p-n Junction

The formation of a p-n junction is critical to the operation of a solar cell. A p-n junction is created when a p-type semiconductor, which has an excess of positive charge carriers (holes), is brought into contact with an n-type semiconductor, which has an excess of negative charge carriers (electrons) [33]. At the interface between the two materials, a built-in electric field is established due to the diffusion of charge carriers across the junction. This electric field helps to separate electron-hole pairs generated by the absorption of photons and drives them towards their respective contacts, thereby generating a photocurrent.

2.5.2. Photocurrent Generation and Collection

When a photon with energy greater than the bandgap of the absorber material is absorbed, it can excite an electron from the valence band to the conduction band, creating an electron-hole pair [33]. This process is known as the generation of photocurrent. The built-in electric field at the p-n junction separates these charge carriers, with electrons moving towards the n-type material and holes moving towards the p-type material. The separated charge carriers are then collected at the contacts, creating a flow of current through an external load [34]. The efficiency of a solar cell depends on the ability of the device to absorb photons, generate electron-hole pairs, separate charge carriers, and collect them at the contacts.

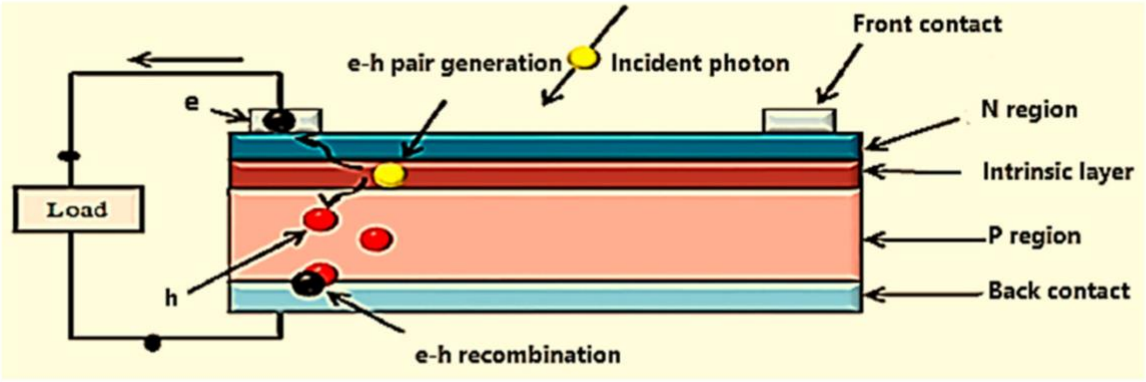

Figure 5. Photocurrent generation and collection in a solar cell. [35]

The performance of a solar cell is often evaluated using the current-voltage (I-V) characteristic, which relates the output current to the voltage across the device under illumination. The I-V curve provides information about the solar cell's open-circuit voltage (Voc), short-circuit current (Isc), fill factor (FF), and power conversion efficiency (PCE) [35]. These parameters are crucial for understanding the performance of a solar cell and optimizing its design.

2.6. Material characterization techniques

To understand the performance of solar cells and improve their efficiency, various characterization techniques are employed. These techniques can be used to investigate the properties of the materials used in the solar cell, such as their composition, structure, and electronic properties, as well as the device's performance under illumination.

2.6.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a powerful technique for imaging and analyzing the microstructure of materials, including thin films used in solar cells [36]. SEM utilizes a focused electron beam to scan the surface of a specimen, generating secondary electrons, backscattered electrons, and X-rays that can be collected to create high-resolution images. The images provide detailed information about the surface morphology, including topography, texture, and particle size distribution [36]. SEM can also be used for elemental analysis through energy-dispersive X-ray spectroscopy (EDS), which helps to determine the composition and stoichiometry of the material [46]. This information is crucial in understanding the properties of thin film materials and optimizing their performance in solar cells.

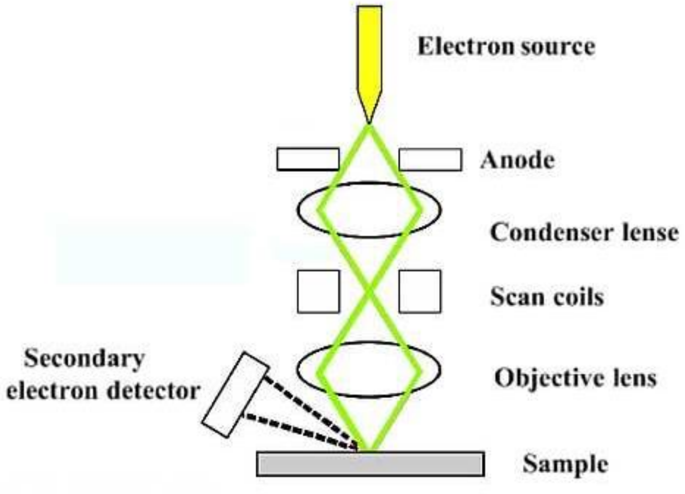

Figure 6. Schematics of SEM. [36]

Scanning Electron Microscopy (SEM) offers several advantages over other imaging techniques, such as optical microscopy, due to its high depth of field, exceptional spatial resolution, and the ability to provide qualitative and quantitative information about the sample [36]. In the context of thin film solar cells, SEM can be particularly useful for investigating various aspects.

One application of SEM is the analysis of surface morphology. SEM can reveal the size, shape, and arrangement of grains or particles on the surface of the absorber layer. This information can help researchers to understand how the film's microstructure impacts its optoelectronic properties and overall performance [36].

Another important application is cross-sectional analysis. By preparing a cross-sectional sample of the solar cell, researchers can use SEM to study the interfaces between different layers, such as the absorber, buffer, and window layers. This can provide insights into the quality of the interfaces and any possible interdiffusion or interfacial reactions that may occur [36].

Additionally, SEM can be combined with Energy-Dispersive X-ray Spectroscopy (EDS) to obtain elemental maps of the sample. This allows for the identification of compositional variations, impurities, or defects in the material, which may affect the performance of the solar cell [36].

Finally, some SEM systems can be equipped with specialized sample holders and environmental chambers, enabling in-situ studies of processes like film growth, selenization, or annealing. This can provide valuable insights into the dynamics of material transformations and the role of processing conditions on the film's properties [36].

In summary, Scanning Electron Microscopy is a versatile and powerful technique for characterizing the microstructure and composition of thin film materials used in solar cells, providing critical information for the optimization of device performance.

For this thesis, the Zeiss EVO-MA15 scanning electron microscope (SEM) with a Zeiss HR FESEM Ultra 55 system was utilized to capture top-view and cross-sectional images of the films, carried out at the Department of Materials and Environmental Technology at Tallinn University of Technology.

2.6.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a powerful analytical technique used to investigate the crystal structure of materials. The technique relies on the interference of X-rays that are scattered by the atoms within a crystal lattice [37]. The fundamentals of XRD can be explained by Bragg's law, which relates the angles at which X-rays are scattered by the crystal lattice to the spacing between the lattice planes and the wavelength of the incident X-rays [37].

When a monochromatic X-ray beam strikes a crystal, the X-rays are scattered by the atoms in the lattice. The scattered X-rays can either constructively or destructively interfere with each other, depending on the path difference between the scattered waves. Constructive interference occurs when the path difference is an integer multiple of the X-ray wavelength, resulting in a diffraction peak in the XRD pattern [37].

Bragg's law, given by the equation:

$$n\lambda = 2d \sin \theta$$

This describes the condition for constructive interference, where n is an integer, λ is the wavelength of the X-rays, d is the spacing between the lattice planes, and θ is the angle of incidence of the X-ray beam [37]. By varying the angle θ and measuring the intensity of the diffracted X-rays, an XRD pattern can be obtained, which provides information about the crystal structure, unit cell dimensions, and atomic positions within the crystal lattice.

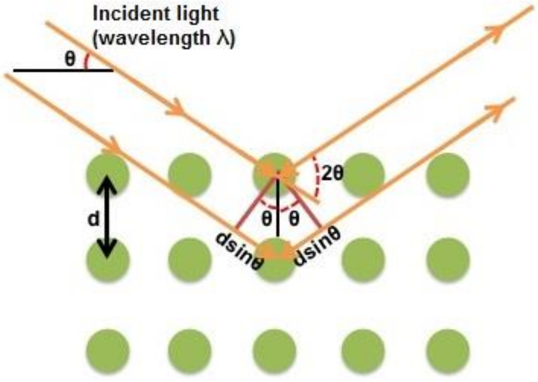

Figure 7. Illustration of the requirements of Bragg's law [37]

XRD is a fundamental technique in the field of crystallography, providing valuable insights into the structural properties of materials. The technique is based on the principles of constructive interference and Bragg's law, allowing researchers to determine the crystal structure and atomic positions in a wide range of materials [37].

In our lab, for the X-ray diffraction (XRD) measurements, a Rigaku Ultima IV diffractometer was used and Rigaku PDXL software was used for the analysis of the XRD patterns. Crystal phases were identified using the data provided by the Joint Committee on Powder Diffraction Standards (JCPDS), with the following data files utilized:

Sb_2Se_3 - JCPDS 01-089-0821
TiO_2 - JCPDS 98-015-4604

2.7. PV device characterization techniques

2.7.1 Current-Voltage (I-V) Characteristics

The current-voltage (I-V) characteristics of a solar cell describe the relationship between the output current density (I) and voltage (V) of the device under illumination. Understanding the I-V curve is crucial for evaluating solar cell performance, as it provides insights into factors such as energy conversion efficiency, open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF).

When a solar cell is exposed to light, the absorbed photons generate electron-hole pairs. The generated electrons and holes are separated by the built-in electric field at the p-n junction, resulting in a photocurrent (J_{ph}). The I-V curve is typically obtained by measuring the output current density and voltage under varying load conditions, from open-circuit to short-circuit [41].

The open-circuit voltage (V_{oc}) is the maximum voltage generated by the solar cell when there is no current flowing through the device. It corresponds to the point where the net current is zero ($J = 0$). V_{oc} is directly related to the quasi-Fermi level splitting and, therefore, is a measure of the quality of the p-n junction and the absorber layer.

The short-circuit current density (J_{sc}) is the maximum current generated when the voltage across the cell is zero ($V = 0$). J_{sc} is directly proportional to the number of photons absorbed by the solar cell and the efficiency of the charge carrier collection process. It is also affected by the optical and electrical properties of the cell, such as absorption coefficient, carrier lifetime, and diffusion length [41].

The fill factor (FF) represents the squareness of the I-V curve and is a measure of the solar cell's performance under operating conditions. It is defined as the ratio of the maximum power (P_{max}) to the product of V_{oc} and J_{sc}:

$$FF = (P_{max} / (V_{oc} * J_{sc})) * 100$$

A high FF indicates a high-quality solar cell with low resistive losses and efficient charge carrier collection [41].

The power conversion efficiency (PCE) is the ratio of the maximum electrical power generated by the cell to the incident light power:

$$PCE = (J_{sc} * V_{oc} * FF) / P_{in} * 100\%$$

PCE depends on the values of V_{oc}, J_{sc}, and FF, and is a key parameter for evaluating solar cell performance [41].
Here is an example of I-V curve of Sb_2Se_3 using two different deposition techniques rapid thermal evaporation (RTE) and VTD:

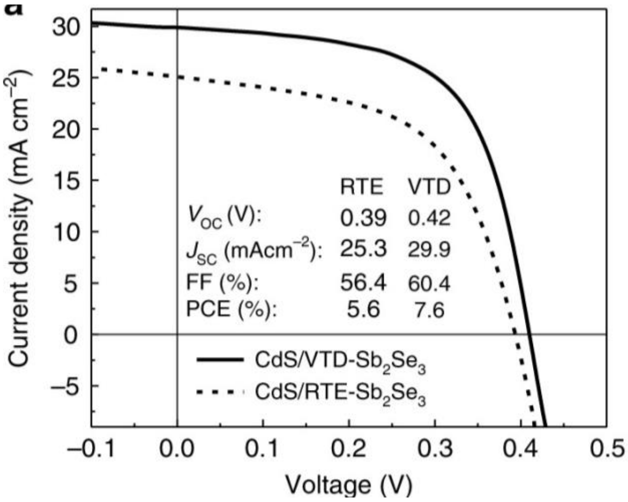

Figure 11. I-V curve of a Sb_2Se_3 (RTE and VTD deposition) solar cell. [14]

2.7.2 External Quantum Efficiency (EQE)

External quantum efficiency (EQE) is a crucial parameter for evaluating the performance of a thin film solar cell. It measures the effectiveness of a solar cell in converting incident photons into collected charge carriers (electrons or holes) as a function of the wavelength of the incident light [42].
EQE is defined as the ratio of the number of charge carriers collected by the solar cell to the number of incident photons at a specific wavelength:

$$EQE(\lambda) = (\text{Number of collected carriers} / \text{Number of incident photons}) * 100.$$

Also, the EQE can be calculated using the following formula:

$$EQE(\lambda) = (1240 * J_{sc}(\lambda)) / (q * P_{in}(\lambda)) * 100\%$$

where λ is the wavelength, $J_{sc}(\lambda)$ is the short-circuit current density at wavelength λ, q is the elementary charge, and $P_{in}(\lambda)$ is the incident light power density at wavelength λ.

By analyzing the EQE spectrum, researchers can identify the wavelength range over which the solar cell is most efficient at converting light into electricity. This information is particularly useful for optimizing the performance of solar cells by improving the light absorption, charge carrier generation, and charge collection processes [42].

EQE measurements can also help identify material and device improvements by highlighting specific regions of the spectrum where the solar cell's performance is limited. For instance, a low EQE at longer wavelengths may indicate poor absorption in the absorber layer or a high density of recombination centers, while a low EQE at shorter wavelengths may be attributed to parasitic absorption or reflection losses [42].

Moreover, EQE measurements are critical for understanding the performance limitations and potential improvements of thin film solar cells. They can provide insights into the effects of various processing techniques, material quality, and device architecture on the overall efficiency of the solar cell [42].

The J-V characteristics and EQE measurements are essential tools for evaluating and optimizing the performance of thin film solar cells. By analyzing these parameters, researchers can gain a deeper understanding of the underlying mechanisms that govern the energy conversion process in these devices and develop strategies to improve their efficiency and stability.

For my thesis, the J-V characteristics of the TiO2/Sb2Se3 solar cells were measured using an AUTOLAB PGSTAT 30 and an Oriel class A solar simulator 91159A (100 mW cm-2, AM1.5) at the Laboratory of Thin Film Chemical Technologies at Tallinn University of Technology and the EQE was measured using a 300 W xenon lamp and an SPM-2 Carl Zeiss-Jena monochromator operating at 30 Hz.

2.8.1. Summary of the theoretical background:

- Sb_2Se_3 thin film solar cells have significant relevance in renewable energy applications.
- Vapor Transport Deposition (VTD) is employed as a fabrication method for Sb_2Se_3 thin films.
- Understanding the basics of semiconductor materials and their properties is crucial for solar cell operation.
- Sb_2Se_3 absorbs light and generates electron-hole pairs, initiating the conversion of solar energy.
- Sb_2Se_3 thin film solar cells consist of specific layers and structures that optimize performance.
- The formation of a p-n junction is essential for the operation of Sb_2Se_3 solar cells.
- Mechanisms exist to create a p-n junction within Sb_2Se_3 films.

- Photocurrent generation in Sb_2Se_3 solar cells results from the conversion of incident photons.
- Factors such as material properties and device design influence photocurrent generation and collection efficiency.
- XRD, SEM, and UV-Vis-NIR Spectrophotometry are used to evaluate the properties of Sb_2Se_3 thin films.
- The J-V curve provides valuable information about the electrical behavior of Sb_2Se_3 solar cells.
- The J-V curve parameters relate to the performance of the solar cell.
- EQE (External Quantum Efficiency) is a measure of the efficiency of light absorption in Sb_2Se_3 solar cells.
- Various factors affect EQE, which ultimately impacts the overall performance of the solar cell.

2.8.2 Aims in the context of the theoretical background:

1. To acquire understanding of working principle of PV devices, properties required for PV device layers, deposition methods, and characterization techniques.
2. To investigate the effects of different VTD substrate temperatures on the structural properties of Sb_2Se_3 thin films and performance of Sb_2Se_3 solar cells and determine optimal processing conditions for the VTD process.

3. Experimental Procedure

The theoretical background of the thesis provided a comprehensive understanding of Sb_2Se_3 thin film solar cell physics, configuration, and operation. This knowledge has allowed us to gain insights into the significance of various factors such as light absorption, electron-hole pair generation, and the formation of p-n junctions in Sb_2Se_3 solar cells. Furthermore, the importance of photocurrent generation and collection efficiency, as well as the role of various characterization techniques such as XRD and SEM, was discussed in detail. These theoretical aspects laid a solid foundation for the experimental investigation of Sb_2Se_3 thin film solar cells fabricated via VTD.

To achieve the stated objective, a series of Sb_2Se_3 thin films and TiO_2/Sb_2Se_3 solar cells will be fabricated using VTD at different substrate temperatures. These samples will be thoroughly characterized using the techniques to evaluate their properties and performance. The correlation between the substrate temperature and the resulting thin film and solar cell characteristics will be investigated, which will provide valuable insights into the optimal fabrication conditions for Sb_2Se_3 thin film solar cells. Following is the structure of the solar cell developed in our lab.

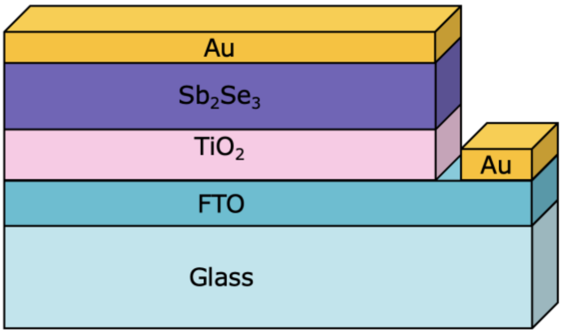

Figure 12: Our Solar Cell Structure

3.1. Fabrication of Sb_2Se_3 thin film solar cells

Substrate Cleaning

The first step in the experimental part of the thesis, substrate cleaning, is a critical process to ensure the proper adhesion and uniformity of the thin films during the VTD process. This step aims to remove any surface contaminants, particles, and organic residues that might negatively affect the film's growth and performance.

To effectively clean the substrates, they were immersed in a cleaning solution composed of potassium dichromate ($K_2Cr_2O_7$), water (H_2O), and sulfuric acid (H_2SO_4). This mixture is a powerful oxidizing agent, which facilitates the removal of organic materials and contaminants from the substrate surface. The substrates were allowed to soak in the cleaning solution for a predetermined period to ensure thorough cleaning.

Following the immersion in the cleaning solution, the substrates were then boiled in distilled water. This step served to remove any residual traces of the cleaning solution and any remaining contaminants from the substrate surface. Boiling in distilled water also helps to minimize the possibility of introducing new contaminants during the cleaning process, as distilled water is free from impurities. Finally, the substrates were dried in hot air.

TiO_2 (buffer layer) deposition

This experimental part of the thesis involved depositing a titanium dioxide (TiO_2) buffer layer on the cleaned substrates using the ultrasonic spray pyrolysis (USP) technique. This buffer layer plays a crucial role in enhancing the performance of the resulting TiO_2/Sb_2Se_3 solar cells by promoting better charge transport and reducing recombination losses.

A precursor solution with a concentration of 0.2M was prepared using titanium isopropoxide (TTIP) and acetylacetone (AA) in a 1:1 molar ratio. This precursor solution was then atomized using an ultrasonic nozzle, generating fine aerosol droplets that were carried by a carrier gas to the heated substrate. The deposition temperature was maintained at 450 °C to ensure the proper formation of the TiO_2 layer and the conversion of the precursor into the crystalline anatase phase of TiO_2.

Following the deposition of the TiO_2 layer, a post-deposition annealing step was performed at 450 °C in air for 30 minutes. This thermal treatment further enhanced the crystallinity and phase purity of the anatase TiO_2 layer, leading to better optoelectronic properties and improved device performance.

The resulting TiO_2 buffer layer had a thickness of approximately 30 nm, which is an optimal thickness for efficient charge transport and minimal recombination losses. The anatase phase of TiO_2 was confirmed through various characterization techniques, ensuring that the desired buffer layer properties were obtained to support the subsequent deposition of Sb_2Se_3 thin films and the fabrication of high-performance TiO_2/Sb_2Se_3 solar cells.

Sb_2Se_3 (absorber layer) deposition

Antimony selenide (Sb_2Se_3) absorber films were deposited by VTD. High-purity (5N, purchased from Alfa-Aesar) Sb_2Se_3 granular powder was used as the source material for the VTD process. The substrates, which already had the TiO_2 buffer layer, were placed at a distance of 10 cm from the Sb_2Se_3 source. The source temperature was maintained at 500 °C to ensure the efficient evaporation of Sb_2Se_3, which was then transported to the substrates in the form of vapor. This VTD process can be shown in Figure 13 below.

To investigate the impact of substrate temperature on the development of Sb_2Se_3 thin films, the temperature of the VTD system was varied, leading to different substrate temperatures of 400, 430, and 460 °C. These temperature variations allowed for the study of their influence on the resulting film properties and solar cell performance.

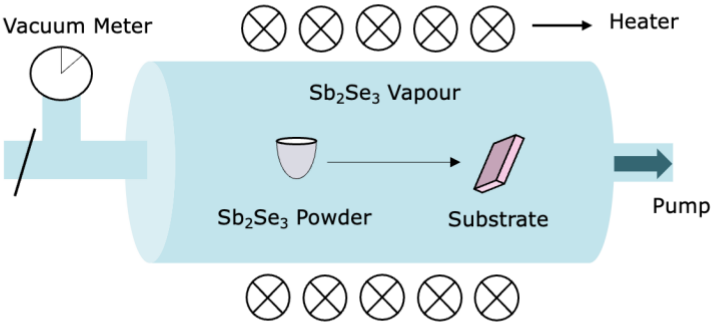

Figure 13: Schematic of the VTD system.

The deposition process was carried out for 5 minutes under a vacuum of approximately 5×10^{-5} mbar, ensuring a controlled environment for the growth of high-quality Sb_2Se_3 films. The resulting absorber layers had a thickness of approximately 800 nm, which is suitable for efficient light absorption and charge generation in the solar cells.

The resulting Sb_2Se_3 thin films were characterized to understand the impact of the substrate temperature variations on their structural, morphological, and optoelectronic properties, providing valuable insights for optimizing the fabrication of high-performance TiO_2/Sb_2Se_3 solar cells.

Back Contact Deposition

The fourth step in the experimental part of the thesis involved the deposition of the gold (Au) layer on the Sb_2Se_3 absorber layer. This step is essential for creating efficient electrical contacts that facilitate charge extraction and current flow in the completed TiO_2/Sb_2Se_3 solar cell.

A thin Au layer was deposited on the surface of the Sb_2Se_3 film, using thermal deposition method, serving as the back contact for the solar cell. In thermal deposition, heating a gold source material, fixed on a tungsten filament, in a vacuum chamber results in the formation of a thin Au film on the surface of Sb_2Se_3. The Au layer has excellent conductivity and good adhesion properties, ensuring a good electrical contact with the Sb_2Se_3 absorber layer.

4. Results and discussion

4.1. Effect of substrate temperature on the structural and optical properties of Sb_2Se_3 thin films

In this study, the effect of substrate temperature on the structural and optical properties of Sb_2Se_3 thin films was investigated. Fig. 14 shows the X-ray diffraction (XRD) patterns of glass/FTO/TiO2/Sb_2Se_3 structures, where the Sb_2Se_3 absorber films were deposited at different source temperatures ranging from 400 to 460 °C. The XRD peaks observed in the diffractograms are characteristic of the orthorhombic crystal phase of Sb_2Se_3 with Pbmn group symmetry. No secondary phases were detected.

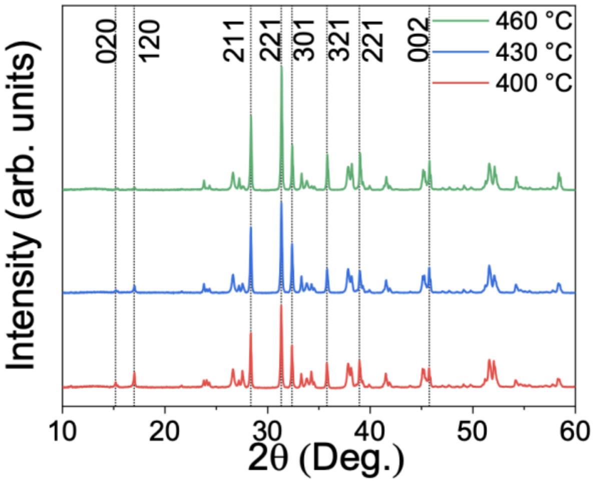

Figure 14: XRD patterns of Sb_2Se_3 on glass/FTO/TiO_2

Since the XRD peak intensities of different samples cannot be compared directly, we calculated texture coefficient (TC) values for the more intense peaks to have a chance to compare the distribution of crystal orientations in different Sb_2Se_3 films. Due to the 1D crystal growth of Sb_2Se_3, TC analysis provides an insight into whether changing a deposition parameter, such as the source temperature, can increase the texture in the desired [001] direction.

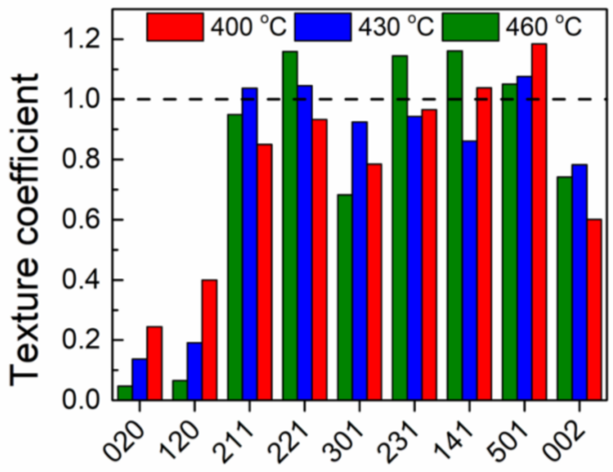

Figure 15: TC patterns of Sb_2Se_3 on glass/FTO/TiO_2

Figure 15 displays the TC values calculated from the XRD patterns using an equation:

$$TC(hkl) = \frac{\frac{I(hkl)}{I_0(hkl)}}{\frac{1}{N}\sum_{i=0}^{N}\frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)}}$$

where I(hkl) is the experimentally measured reflection intensity of a (hkl) crystal plane, I0(hkl) is the reference intensity for the corresponding crystal plane acquired from the reference pattern (JCPDS Card No. 15–0861), and N is the number of peaks used in the calculation. First, it is important to note that all three Sb_2Se_3 films show lower TC values for the (002) peak than for different (hk1) planes, which refer to tilted grains that have an angle with the [001] direction. Such grains are still regarded as beneficial for carrier transport, although grain boundaries could be in the way of vertical carrier transport. Notably, the TC values for the (020) and (120) planes were higher for the Sb_2Se_3 film deposited at 400°C compared to those at 430 °C and 460 °C. This might indicate that the Sb_2Se_3 film at 400°C had more grains lying horizontally, which is considered unfavorable for efficient carrier transport. In contrast, the Sb_2Se_3 film at 430 °C exhibited the highest TC value for the (211) peak, while the film at 460 °C demonstrated the highest TC value for the (221) peak.

Figure 16 and figure 17 show the top-down and cross-sectional SEM images of the Sb_2Se_3 film deposited at 460 °C on the TiO2/FTO/glass substrate. What can be seen from both images is that the Sb_2Se_3 film has formed a compact structure with large grains. Large grain morphology is desired as it reduces the number of grain boundaries, which are known to act as recombination centers for charge carriers. By minimizing grain boundaries, the films can exhibit enhanced charge transport properties, leading to

improved solar cell performance. The film can be further optimized because the grains sizes vary and none of them span the entire absorber width, which would allow unimpeded carrier transport to adjacent device layers.
Based on the prior knowledge of Nicolae Spalatu's research group at our Lab in working with deposition of CdTe, Sb_2Se_3 and Sb_2Se_3 thin films by CSS. It is known that substrate temperature has strong influence on the grain growth in thin films. At higher substrate temperatures, less nuclei remain on the surface, which start evolving into larger islands.

Higher substrate temperatures also provide more energy for the material transfer between these islands, which can eventually coalesce into a single grain. Lowest minimum energy principle favors coalescence since it lowers the surface energy of the joining islands. Therefore, it is expected that Sb_2Se_3 films produced at substrate temperatures of 400 °C and 430 °C have smaller grain morphologies and larger grain boundary densities. Due to lower temperatures, there is also higher probability for the emergence of voids.

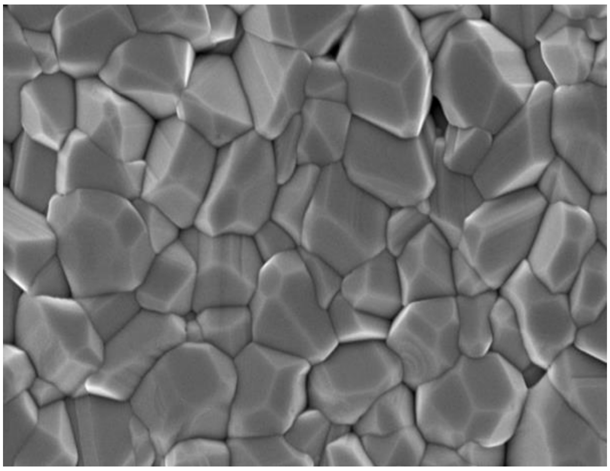

Figure 16: Surface SEM image of glass/FTO/TiO2/Sb_2Se_3, where Sb_2Se_3 film was deposited at 460 °C.

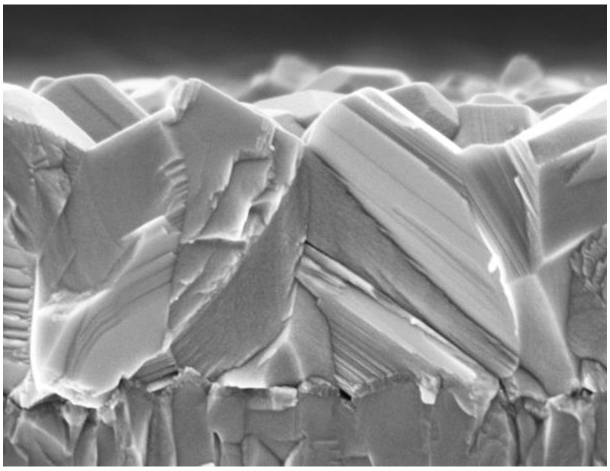

Figure 17: Cross-sectional SEM images of glass/FTO/TiO2/ Sb_2Se_3, where Sb_2Se_3 film was deposited at 460 °C.

After material characterization of Sb_2Se_3 films, we completed the PV devices employing the three Sb_2Se_3 films to see how they perform.

4.2. Effect of substrate temperature on the device properties of Sb_2Se_3 thin film solar cells

To evaluate solar cell performance, J-V characteristics were measured for the three Sb_2Se_3 PV devices, as shown in Fig. 17. Table 1 shows the device properties such as the open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and power conversion efficiency (PCE). The results show that the substrate temperature has an effect on the solar cell performance. It can be seen that the device with Sb_2Se_3 film deposited at substrate temperature of 450 °C (Sb_2Se_3 -460 °C) performs the best, with largest JSC, VOC, and ultimately PCE of 3.8%.

As compared to devices with Sb_2Se_3 films deposited at 400 °C (Sb_2Se_3 -400 °C) and 430 °C (Sb_2Se_3 -430 °C), has a considerably larger VOC at 340 mV. This points to a better interface quality between the TiO_2 buffer and the Sb_2Se_3 absorber. Similarly, Sb_2Se_3 -460 °C device has JSC of 27.5 mA cm-2, which is more than the 23.3 mA cm-2 or 24.4 mA cm-2 obtained for Sb_2Se_3 -400 °C and Sb_2Se_3 -430 °C cells, respectively. It is also worth noting that device properties show gradual increase with substrate temperature. This suggest the absorber quality gets better with higher substrate temperature, and can be associated with larger and more compact grain morphology achieved for the Sb_2Se_3 -460 °C film

No.	T_{sub} (°C)	Solar cell properties			
		V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
1.	400	241	23.3	44.8	2.5
2.	430	271	24.4	46.3	3.1
3.	**460**	**340**	**27.5**	**40.4**	**3.8**

Table 1: Solar Cell Properties with respect to Substrate Temperature.

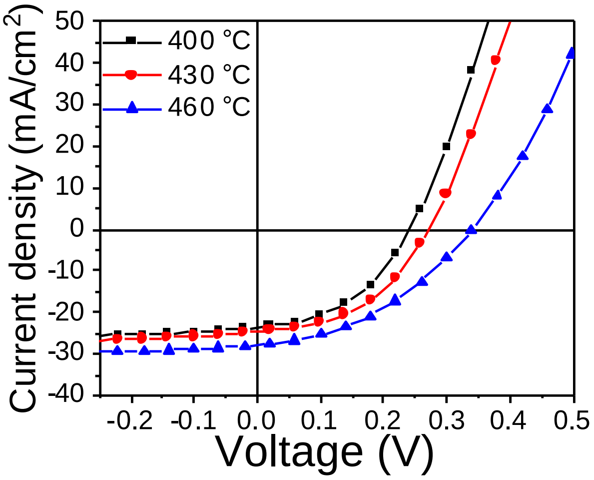

Figure 18: Current Density vs Voltage graph.

The EQE of a solar cell provides a measure of how effectively the device can convert incident light photons of different wavelengths into electricity. The EQE of the three devices is depicted in Fig. 18. Similar to J–V curves, device with the Sb_2Se_3-460 °C absorber shows best photoresponse in the entire active wavelength region from 350 to 1050 nm. Best EQE response gain comes from the visible light range, achieving 80% efficiency. Again gradual improvement can be seen, with Sb_2Se_3-430 °C solar cell showing slightly better photoresponse than the Sb_2Se_3-400 °C device. This indicates that the absorber layer's optical properties were enhanced at higher deposition temperatures, resulting in improved absorption and carrier generation capabilities.

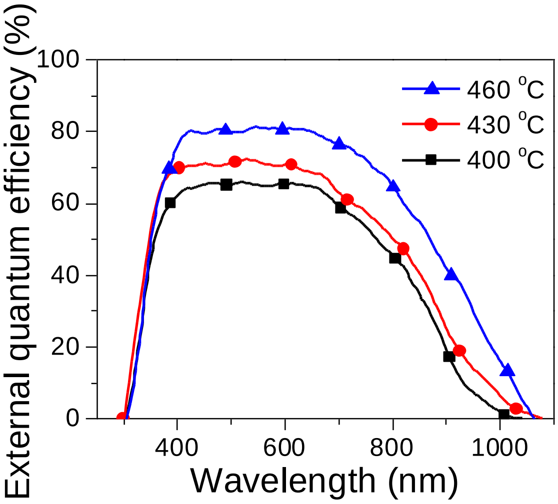

Figure 19: EQE vs Wavelength graph.

The bandgap energy of the Sb_2Se_3 material can be estimated from the modified EQE plot, as shown in Figure 19 [44]. The linear region of this graph can be extrapolated to the x-axis to estimate the bandgap. Based on the EQE measurements, the bandgap of Sb_2Se_3 is estimated to be around 1.28 eV.

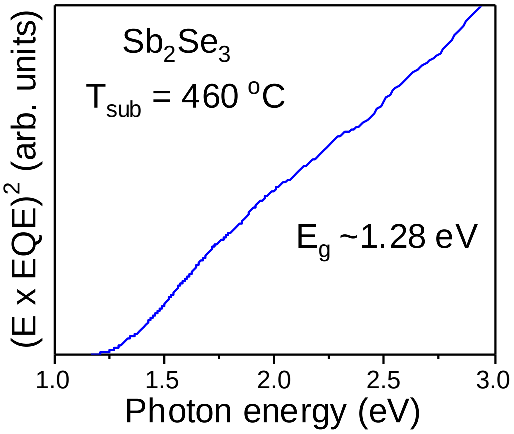

Figure 20: Sb_2Se_3 bandgap energy of 1.3 eV calculated from a modified EQE plot.

In short, the impact of substrate temperature during the VTD process plays a significant role in determining the performance of the Sb_2Se_3 thin films and the resulting solar cells. By carefully controlling the substrate temperature, it is possible to optimize the structural, morphological, and optoelectronic properties of the Sb_2Se_3 absorber layer, which in turn leads to improved solar cell performance.

5. Conclusion

This thesis aimed to investigate the impact of substrate temperature during the vapor transport deposition (VTD) process on the properties of Sb_2Se_3 thin films and the performance of TiO_2/Sb_2Se_3 solar cells. The focus was on developing a comprehensive understanding of the relationship between the substrate temperature, the structural and morphological properties of the thin films, and the resulting solar cell performance.

The literature review provided an overview of the fundamental concepts and analytical techniques used in this study. The fabrication processes and characterization techniques for thin film solar cells were discussed, with a particular emphasis on Sb_2Se_3-based devices.

In the experimental section, a detailed description of the fabrication process of the solar cells was given. This included the cleaning of the substrates, the deposition of the TiO_2 buffer layer via ultrasonic spray pyrolysis, and the deposition of the Sb_2Se_3 absorber layer via VTD at different substrate temperatures. The fabrication process concluded with the deposition of the Au and In contacts.

The results indicated the impact of substrate temperature on the structural and optical characteristics of Sb_2Se_3 thin films. X-ray diffraction (XRD) analysis of glass/FTO/TiO_2/Sb_2Se_3 structures, with Sb_2Se_3 absorber films deposited at temperatures ranging from 400 to 460 °C, revealed primary peaks corresponding to the orthorhombic crystal phase of Sb_2Se_3 with Pbmn group symmetry. Texture coefficient (TC) calculations were employed to assess the crystal orientation variation, providing insights into the distribution of crystal orientations within the Sb_2Se_3 films. The XRD analysis confirmed the absence of secondary phases in Sb_2Se_3 for all samples. The TC values further elucidated the structural properties by revealing the crystal orientation distribution within the Sb_2Se_3 thin films.

SEM image revealed a compact structure composed of large grains, indicating good film quality. The morphological properties of the Sb_2Se_3 films, such as grain size and uniformity, improved with increasing substrate temperature, which further enhanced the performance of the solar cells.

The performance of the solar cells, as evaluated by J-V characteristics and EQE measurements, also improved with increasing substrate temperature. Notably, the V_{oc}, J_{sc}, and PCE all increased with substrate temperature. The fill factor (FF) increased up to 430 °C but showed a slight decrease at 460 °C, indicating that a balance must be struck to optimize the performance of the solar cells.

In conclusion, this study underscores the importance of substrate temperature during the VTD process in the fabrication of Sb_2Se_3 thin films and TiO_2/Sb_2Se_3 solar cells. The results provide a basis for further studies aimed at optimizing the performance of Sb_2Se_3-based solar cells and contribute to the broader efforts in developing efficient and cost-effective thin film solar cells. Future work could explore the impact of other process parameters on the properties of Sb_2Se_3 thin films and the performance of the resulting solar cells.

6. Summary

This thesis embarked on a comprehensive exploration of the relationship between the substrate temperature during Vapor Transport Deposition (VTD) and the properties of Sb_2Se_3 thin films, as well as the performance of TiO_2/Sb_2Se_3 solar cells. The objective was to elucidate the role of substrate temperature in determining the structural, morphological, and optoelectronic properties of the thin films and the resultant solar cell characteristics.

The journey commenced with an extensive literature review, which laid the groundwork for understanding the theoretical concepts and analytical techniques pertinent to this study. The focus was primarily on the fabrication processes and characterization methods for thin film solar cells, with special emphasis on those based on Sb_2Se_3.

In the experimental segment of the thesis, an in-depth description of the solar cell fabrication process was presented. This included the cleaning of the substrates, the deposition of the TiO2 buffer layer through ultrasonic spray pyrolysis, and the deposition of the Sb2Se3 absorber layer via VTD at different substrate temperatures. The process concluded with the deposition of the Au contacts.

The results investigated the impact of substrate temperature on the structural and optical properties of Sb_2Se_3 thin films. XRD analysis confirmed the orthorhombic crystal structure, while TC and SEM analysis revealed favorable crystal orientations and compact grain morphology. These findings provide valuable insights for optimizing the performance of TiO_2/Sb_2Se_3 solar cells.

The study concluded that substrate temperature during the VTD process is a critical factor in fabricating Sb_2Se_3 thin films and TiO_2/Sb_2Se_3 solar cells. The findings open up avenues for further research aiming to optimize the performance of Sb_2Se_3-based solar cells and contribute to the larger goal of developing efficient and economical thin film solar cells.

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