

Investigation of the optical properties of $\text{Cu}_2\text{ZnSnSe}_4$ and detection of the secondary phases in $\text{Cu}_2\text{ZnSnSe}_4$ solar cell absorbers by spectroscopic ellipsometry

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Contents

Abstract	v
Kurzfassung.....	vi
Preface.....	vii
Chapter 1: Introduction	1
Chapter 2: Material.....	3
2.1 Synthesis of $\text{Cu}_2\text{ZnSnSe}_4$ absorber	3
2.2 Formation of secondary phases.....	4
2.3 Impact of secondary phases on solar cell performance.....	8
2.4 Detection of secondary phases in $\text{Cu}_2\text{ZnSnSe}_4$ thin films.....	11
Chapter 3: Spectroscopic ellipsometry.....	13
3.1 Spectroscopic ellipsometry	13
3.1.1 Polarized light.....	13
3.1.2 Surface Roughness	17
3.1.2.1 Effective Medium Approximation	18
3.1.3 Film Thickness	19
3.1.4 Optical constants	20
3.2 Oscillators	21
3.2.1 PSEMI oscillators	21
3.3 Semiconductors.....	24
3.3.1 Optical transitions in semiconductors.....	24
Bibliography.....	28
Chapter 4: Detection of a MoSe_2 secondary phase layer in CZTSe by spectroscopic ellipsometry.....	35
Chapter 5: Optical properties of $\text{Cu}_2\text{ZnSnSe}_4$ thin films and identification of secondary phases by spectroscopic ellipsometry	43
Chapter 6: Influence of Cu-Zn disorder in $\text{Cu}_2\text{ZnSnSe}_4$ absorbers on optical transitions: A spectroscopic ellipsometry study.....	59
Chapter 7: Conclusion.....	73
Acknowledgement.....	74
Disclaimer	75

Abstract

The interest in quaternary compound semiconductor (SC) $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) has been rapidly increasing as an alternative absorber to the current thin film technologies. Their direct band gap and high absorption coefficient ($>10^4 \text{ cm}^{-1}$) make them a good candidate in solar cell technology. The band gap of CZTSSe compound SC is varying from 1.5 eV (pure S-based $\text{Cu}_2\text{ZnSnS}_4$) to 1.0 eV (pure Se-based $\text{Cu}_2\text{ZnSnSe}_4$). The band gap tunability of this material is also beneficial for multi-junction technology. Besides, lower toxicity and higher earth abundance, these are also promising for low cost and clean solar cell technology. However, the chemical and electronic nature of this material is challenging, i.e. co-existence of undesired secondary phases, band gap fluctuations, open circuit voltage V_{oc} -deficit, low short circuit current density J_{sc} , etc..

The aim of this thesis is based on three motivations; the first one is the investigation of the optical properties of CZTSe absorber, and the second one is the identification of the secondary phases with finding their locations in CZTSe absorber and the last one is that these two steps should be done by a non-destructive tool. Therefore, Spectroscopic Ellipsometry (SE) was applied for all examined CZTSe absorbers and the MoSe_2 sample as a main characterization tool since SE is a powerful technique to characterize the optical properties of a thin film. For SE data analysis, different optical model approaches were discussed with their results.

Keywords: CZTSe quaternary compound semiconductor (SC), unwanted secondary phases, spectroscopic ellipsometry (SE), optical model.

Kurzfassung

Das Interesse an den Halbleiter (HL) aus den quaternären Verbindungen $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) wächst schnell, da sie eine alternative als Absorbermaterial für die aktuellen Dünnschicht-Solarzellen darstellt. Aufgrund ihrer direkten Bandlücke und ihres hohen Absorptionskoeffizienten ($>10^4\text{cm}^{-1}$), sind sie gute Kandidaten für Solarzellentechnologie. Die direkte Bandlücke des Verbindungs-HL CZTSSe variiert von 1.5 eV (rein S-basiertes $\text{Cu}_2\text{ZnSnS}_4$) bis 1.0 eV (rein Se-basiertes $\text{Cu}_2\text{ZnSnSe}_4$). Die Abstimmbarkeit der Bandlücke dieses Materials ist auch von Vorteil für Multi-JunctionTechnologien. Darüber hinaus sind diese Verbindungen aufgrund ihrer niedrigeren Toxizität und höherer Häufigkeit ihrer Elemente als günstige und saubere Solarzellentechnologie vielversprechend. Dennoch gibt es Herausforderungen bei den chemischen und elektronischen Eigenschaften dieses Materials, z.B. die Koexistenz ungewünschter Sekundärphasen, Bandlückenfluktuationen, Leerlaufspannungsdefizit, niedriger Kurzschlussstrom, etc.

Das Ziel dieser Arbeit basiert auf drei Hauptmotivationen erstens die Untersuchung der optischen Eigenschaften vom $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) Absorber, zweitens die Erkennung von Sekundärphasen und ihrer Position im CZTSe Absorber und drittens die ersten zwei Schritte auf zerstörungsfreie Weise in einem einzelnen Aufbau durchzuführen. Deswegen wurde spektroskopische Ellipsometrie (SE) auf alle untersuchten CZTSe Absorber und auf die MoSe_2 Proben angewendet, da SE eine mächtige Methode für die Charakterisierung der optischen Eigenschaften dünner Schichten ist. Für die SE-Analyse werden unterschiedliche optische Modelle und ihre Ergebnisse vorgestellt und diskutiert.

Keywords: CZTSe quaternary compound semiconductor (SC), unwanted secondary phases, spectroscopic ellipsometry (SE), optical model

Preface

This work is a cumulative type of dissertation to achieve the German academic degree of a doctor of natural sciences (Dr. rer. nat.). It is based on three manuscripts which are published in or at least submitted to peer-review journals from the field of applied physics. The presented articles are given in Chapter 4 – 6. The common theme of these articles is the characterization of the optical properties of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) absorber and the detection of the undesired phases in CZTSe material by spectroscopic ellipsometry (SE). The investigated CZTSe samples were provided by University of Luxembourg and the MoSe_2 sample was supplied by the company AVANCIS GmbH, Germany.

The first chapter provides an overview of why we work on CZTSe quaternary compound semiconductor (SC). In the second chapter, we focus on the synthesis of CZTSe material, and unwanted secondary phases in CZTSe material with their effect on the solar cell efficiency. Additionally, the challenges of detection of these phases were discussed.

SE was applied as a main characterization tool in order to investigate the fundamental optical properties of the solar cell relevant CZTSe absorbers including interband transitions and the identification of secondary phases in CZTSe absorbers. Therefore, SE was introduced in Chapter 3.

In Chapter 4, the detection of the MoSe_2 layer at the back side of the CZTSe absorber with its optical constants, CZTSe's optical constants and the extraction of MoSe_2 thickness by applying a comparative optical model for SE data analysis were exhibited.

In Chapter 5, an improved optical model for SE data analysis was presented to investigate the optical constants of CZTSe absorbers, i.e., refractive index and the extinction coefficient which were used to extrapolate the band gap of CZTSe materials. Additionally, the comprehensive optical model allows us to detect the secondary phases not only at the back side of the CZTSe absorbers (MoSe_2 and ZnSe secondary phases) but also at the front side of the CZTSe absorbers (ZnSe secondary phase) and within the CZTSe absorbers (ZnSe secondary phase).

As a final step, SE was performed to extrapolate not only the fundamental band gap values but also further optical transitions in CZTSe material. The effect of Cu-Zn order in CZTSe absorber on the optical transitions was investigated by using SE. To provide different degree of Cu-Zn order, a systematic study was accomplished by applying different heat treatment and different time on CZTSe material. Additionally, a new optical model approach was demonstrated (Chapter 6).

The findings of the three articles are summarized as a conclusion in Chapter 7.

Chapter 1

Introduction

Silicon (Si) based solar cells dominate the major part of the photovoltaic (PV) market due to the availability in the earth crust and high-quality of the mass production. However, the demands of finding the new low-cost and earth abundant material for solar cell technologies have been increasing due to the concern about the production expense and the difficulties in the refinement of Si [1,2]. Thus, compound SC thin films such as CdTe and CuInGa(S,Se)₂ (CIGSSe) have become an alternative to Si-based solar cells. The PV market has been filled rapidly by these new technologies over the years. The world record efficiencies for CIGS and CdTe are 22.6 % and 22.1%, respectively [3,4]. The achievement of cell efficiency of these solar cells buries the fact of the scarcities of Indium (In) and Tellurium (Te) and the toxicity of Cadmium (Cd). Thus, the manufacturing costs become more and more day by day with these reasons. Therefore, scientists have continued to search different quaternary compound SC thin films to overcome these issues. One of the potential candidate is Cu₂ZnSn(S,Se)₄ (CZTSSe) quaternary compound SC material due to the earth abundance, non- toxic and low material costs. Therefore, In and Ga metals were replaced by zinc (Zn) and tin (Sn) metals by satisfying the octet rule. The compound SCs are denoted by the positions of the atoms in the periodic table. Fig. 1.1 represents the formation of stoichiometric I₂-II-IV-VI₄ compound SCs. Fig. 1.2 represents the crystal structure of elemental Si SC and compound SCs which are derived from II-VI compound SCs.

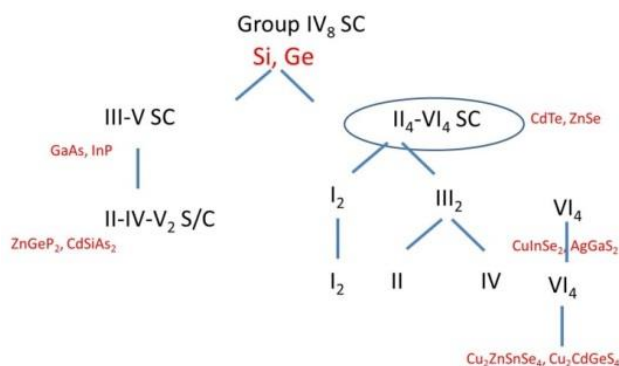


Fig. 1.1 Diagram for how to select the elements from the periodic table for making compound SC absorber under the stoichiometric conditions

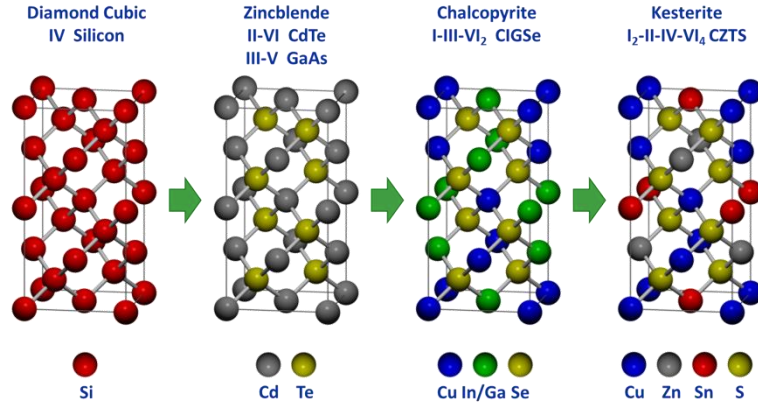


Fig. 1.2 Crystal structures of elemental and compound semiconductor materials⁵

The optoelectronic properties of CZTSSe make a good candidate for the next generation thin film solar cells as well as low material costs, non-toxicity and earth abundance. CZTSSe compound SC materials have direct band gap and high absorption coefficient ($>10^{-4} \text{ cm}^{-1}$). The band gap of CZTSSe compound SC varies from 1.5 eV to 1.0 eV with the varying S/Se content [6-10]. However, the maximum reported efficiency for the CZTSSe SC thin film in the laboratory solar cell is 12.7% [11]. The solar cell efficiency achieved is quite lower than the other competitive cells. One of the major restrictions is the formation of unwanted secondary phases which are detrimental to solar cell performance [12-13]. One of the other issues is the Cu-Zn plane disorder which leads to band gap fluctuations [14-15] and might affect transport properties of the CZTSe material [16,17]. In this thesis, we focus on optical properties of CZTSe material, the detection of the unwanted minor phases in CZTSe absorber (Chapter 4 and Chapter 5) and the influence of the Cu-Zn disorder in CZTSe material on the optical transitions (Chapter 6).

Chapter 2

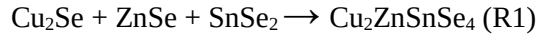
Material

In this chapter, we will focus on the formation of CZTSe material, the undesired secondary phases in CZTSe absorber and their impacts on the solar cell efficiency.

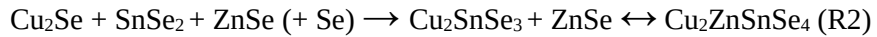
2.1 Synthesis of $\text{Cu}_2\text{ZnSnSe}_4$ absorber

The manufacturing process of multinary compounds usually consists of a heat treatment under reactive atmosphere to form the wanted phases for solar cell devices. One of the main reasons for the heat treatment is to provide enough energy for the atoms, to diffuse to their equilibrium positions, and to overcome the kinetic barriers to achieve the most thermodynamically stable phase for the formation of the desired phases. Different fabrication methods have been widely worked to synthesize CZTSSe absorbers in the literature [11,18-31]. The synthesis of chalcogenide compound SC absorbers can be done either by vacuum based or non-vacuum based techniques as chemical deposition methods. These different fabrication routes have their advantages and disadvantages. However, they will not be discussed here as it is out of the scope of this thesis. For chalcogenide based solar cell absorbers typically required temperature is in the range of 400 °C and 600 °C [32].

There are different reaction paths to synthesize the CZTSe absorber as shown below [33];

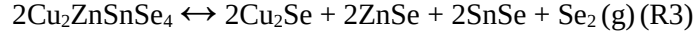


or

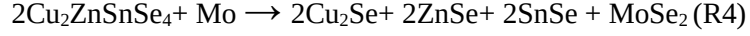


However, the synthesis of pure CZTSe is not as easy as seen in the formation reaction. Since the formation of single CZTSe phase is complex and suffers from Se-loss during the fabrication process due to the relative instability of Sn^{IV} oxidation state compared to Sn^{II} state in Sn-Se system [33]. Another loss mechanism is the Sn-loss which occurs under the high temperature [34]. In addition, the high vapor pressure of SnSe may lead to Sn loss [32]. However, these loss

mechanisms might be compensated by adding Se and SnSe during the annealing step [32]. The predicted decomposition reaction can be written as below [33];



Another issue is the decomposition of the CZTSe caused by the contact with a Mo-substrate. The decomposition reaction is as below [33]:



We can conclude that the pure CZTSe phase formation is more complex and the formation of binary or ternary minor phases is very likely due the thermodynamic instability of CZTSe. To deposit a pure single CZTSe phase under the optimal stoichiometry for the high efficiency PV device, it is needed to follow an effective strategy during the fabrication process to control and compensate the formation of secondary phases. The formation of secondary phases will be discussed in next section in detail.

2.2 Formation of Secondary phases

Olekseyuk et al. has studied the phase diagram for Cu-Zn-Sn-S system [35]. Fig. 2.1 shows the Cu_2S - ZnS - SnS_2 pseudo-ternary phase diagram. The circle which is labelled as 1 in the Fig. 2.1 shows the stoichmetric point for the formation of S-based kesterite structure CZTS quaternary compound SC. The stoichmetric point for CZTS is very narrow and the coexistence of the other phases is very likely. In this thesis, the investigated samples are Se-based kesterite structure CZTSe. However, CZTSe phase diagram has not been studied extensively as CZTS. Nevertheless, it is expected to have similar phase diagram to CZTS quaternary compound SC.

670 K
1) $\text{Cu}_2\text{ZnSnS}_4$

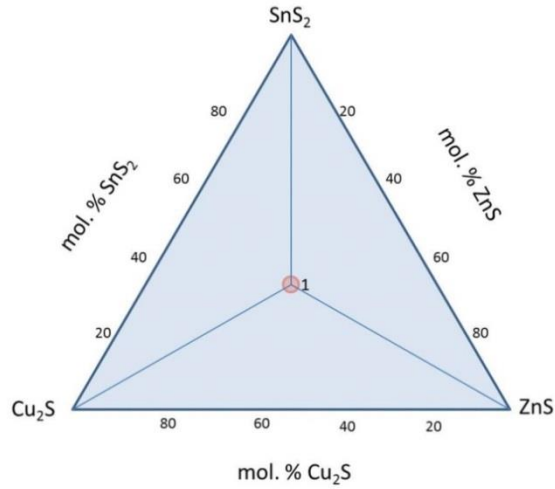


Fig. 2.1 The pseudo-ternary phase diagram for Cu-Zn-Sn-S system. Adapted from Ref. 35

Fig. 2.2 shows the phase diagram for Se-based kesterite CZTSe which is very similar to S-based kesterite [36]. There are different regions to describe the different equilibrium conditions and compositions given in Fig. 2.2, i.e., region 1: stoichiometric point for pure CZTSe, region 2: CZTSe is with SnSe_2 and ZnSe , region 3: CZTSe is with CTSe and SnSe_2 , region 4: CZTSe is with CTSe and Cu_2Se , and region 5: CZTSe is with Cu_2Se and ZnSe , respectively.

670 K
1) $\text{Cu}_2\text{ZnSnSe}_4$

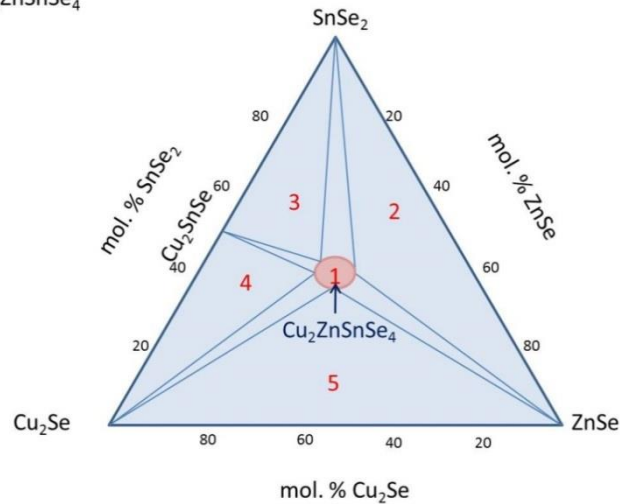


Fig. 2.2 The quasi ternary phase diagram of the Cu_2Se - ZnSe - SnSe_2 system: adapted from Ref. 36

As discussed above, the region for the formation of pure CZTSe is very small and the formation of binary or ternary phases is very likely due to the narrow region of single phase CZTSe and thermodynamic instability of CZTSe.

Each secondary phase has a specific temperature to form in the reaction chain and the temperature required for different secondary phases has been studied extensively [32-33]. Fairbrother et al. reported that ZnSe binary phase appears at very low temperature (down to 300 °C) [37], Chandra et al. showed that the ternary phase Cu_2SnSe_3 (CTSe) [38] can form at temperature down to 150 °C during the co-evaporation process and Altamura et al. noted that SnSe can form at low temperature and persisting at temperature higher than 500 °C [32]. The possibility of the formation of binary or ternary phases is related to the compositional structure of CZTSe material. Simply, to predict the expected secondary phases within the CZTSe material, it is necessary to know the compositional structure of the CZTSe material.

Table 2.1 summarizes the possible secondary phases under the different compositional conditions [32].

Table 2.1. Possible secondary phases with the different compositions discussed in Ref. 32

The description of the composition	Possible binary/ternary phases
Cu-poor	$\text{Cu}_2\text{ZnSn}_3\text{Se}_8 + \text{ZnSe}$
Cu-rich	Cu_2Se
Zn-poor	$\text{Cu-Sn-Se} + \text{Cu}_2\text{ZnSn}_3\text{Se}_8 / \text{Cu}_2\text{Se}$
Zn-rich	ZnSe
Sn-poor	$\text{Cu}_2\text{Se}, \text{ZnSe}$
Sn-rich	$\text{Cu}_2\text{ZnSn}_3\text{Se}_8$

These minor phases can be located anywhere in a typical solar cell device. D. Berg illustrated the possible location scenarios of these unwanted secondary phases in his Ph.D. thesis [39]. Fig. 2.3 shows the possible scenarios for the possible location of secondary phases in the CZTSe solar cell device.

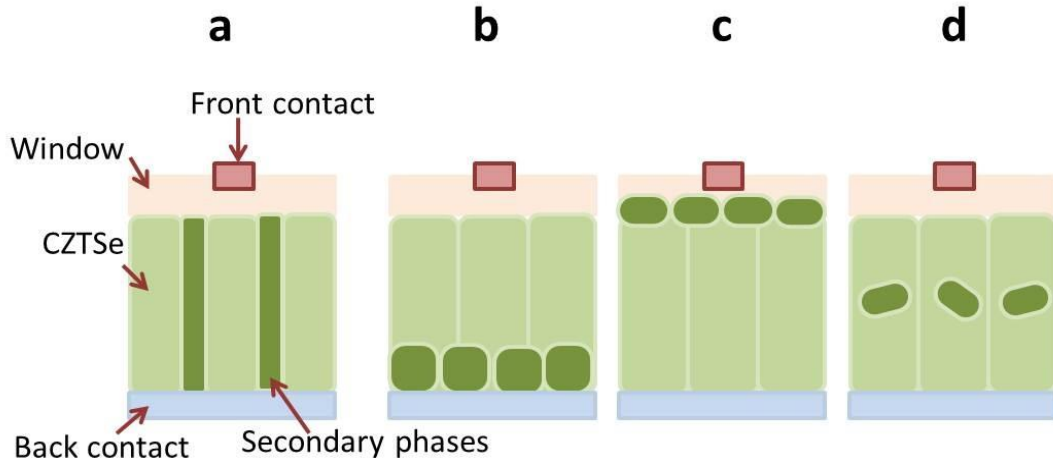


Fig. 2.3 Possible location for secondary phases in CZTSe solar cell device (adapted from Ref. 39)

These undesired minor phases can be located a) in grain boundaries, b) at the back contact of the absorber, c) at the front of the absorber layer, d) within the absorber layer, respectively. Different location of the secondary phases in CZTSe solar cell causes different effect on the cell performance. This will be discussed in detail in Section 2.3. The minor phases in CZTSe can be summarized as below,

- a. **Cu-Se phases:** Cu-based secondary phases usually form under the Cu-rich conditions. The reports show that the band gap of this phase is in between 1.2 and 2.0 eV [32,40]. It has been reported that Cu-Se phase has a p-type nature and indirect band gap [41]. As reported that Cu diffuses from absorber layer to the buffer layer which kills the p-n junction due to the misfit of Cu chemical potential between Cu_xSe and CdS [42]. Additionally, the interface in between Cu_xSe and CdS causes highly concentrated positive charge traps [43]. Thus, this secondary phase is harmful if it locates at the front side of the absorber layer.
- b. **Sn-Se phases:** Sn related secondary phases (SnSe and SnSe_2) are more likely to form during the selenization process. This formation usually takes place under the Cu-poor condition and also Zn-poor, Sn-rich condition. They may occur at the back side of the absorber layer, in the bulk or in the front side of the absorber layer [37,44,45]. SnSe secondary phase has an orthorhombic structure and the band gap is in between 0.9-1.3 eV, in addition to, it has p-type nature SC, SnSe_2 has a hexagonal structure and the band gap varies in the range of 0.96-1.03 eV with n-type nature SC [32]. If the phase

locates in the CZTSe/CdS interface, sub-energy levels may form and cause a reduction in V_{oc} [44] and in some cases, a decrease in J_{sc} [46].

- c. **Zn-Se phase:** ZnSe is an intrinsic SC and can be doped either p-type or n-type SC [32]. However, it is hard to achieve p-type doped ZnSe [47]. Undoped ZnSe SC has been found highly resistive [48]. The optoelectronic properties of ZnSe have been reported that the band gap is ~ 2.7 eV with the high absorption coefficient $\sim 10^4 \text{ cm}^{-1}$ [32]. ZnSe secondary phases occur as the most common phase during or after the selenization process of CZTSe absorber material [49-51]. This secondary phase can be found at the back contact, at the front contact or at the grain boundaries of CZTSe material and also as a network [52-56]. Depending on the position of the ZnSe secondary phase in CZTSe, the solar cell performance, V_{oc} and J_{sc} can be affected in a different way. The crystal structure of ZnSe is similar to CZTSe material and their lattice parameters are also similar. D. Colombra et al. reported that ZnSe behaves like a current blocker and reduces the J_{sc} , in addition, increases the series resistance [57].
- d. **Cu-Sn-Se phase:** There are several phases within Cu-Sn-Se systems in the literature, i.e., Cu_2SnSe_3 , Cu_3SnSe_4 , Cu_4SnSe_4 , $\text{Cu}_4\text{Sn}_7\text{Se}_{16}$, $\text{Cu}_{10}\text{Sn}_2\text{Se}_{13}$, $\text{Cu}_4\text{Sn}_3\text{Se}_8$, $\text{Cu}_4\text{Sn}_{15}\text{Se}_{32}$, $\text{Cu}_5\text{Sn}_2\text{Se}_7$ [58-61]. However, the most persisting phase is Cu_2SnSe_3 (CTSe) [32]. There are discrepancies in reported band gap of CTSe in the literature, varying from 0.49 eV to 0.9 eV [32,44,62]. This minor phase can be formed in CZTSe material during or at the end of the selenization process, usually at the surface of Cu-poor Zn-rich CZTSe material [32] and creates defect levels due to the lower band gap of the material. Additionally, it causes a decrease in V_{oc} [44] and increase in recombination rate [63].

2.3 Impact of secondary phases on solar cell performance

Secondary phases can be located anywhere in the solar cell device as illustrated in Fig. 2.3. Different locations of these unwanted phases in solar cell device have different influence on the solar cell performance. In this section, possible cases will be discussed.

- a. If the secondary phases are located at the grain boundaries, an alternative current flow occurs due to the shunt resistance and the performance of the solar cell will be killed [43].
- b. If the secondary phases are present at the back side of the CZTSe absorber, the series resistance will increase due to the high resistivity of the minor phases. This will affect

the solar cell performance. However, if the minor phases are not highly resistive, the solar cell performance will not be damaged as the other case affects [49-50].

- c. If the position of the secondary phase is in between the CZTSe absorber layer and the buffer layer (usually CdS), the band alignment of the solar cell will be affected. If the nature of the secondary phases is p- type and has a lower band gap than the absorber layer, it will reduce the open circuit voltage and not be that much harmful for the solar cell performance. However, if the band gap of the secondary phases is larger than that of CZTSe absorber, it might cause a potential barrier for the charge carrier, not favorable for the solar cells [32,64].
- d. If the secondary phases are located within the CZTSe absorber, a lower volume of CZTSe will affect the recombination of charge carriers [65].

The secondary phases have different impact on the solar cell performance according to the location in the device. However, this is not the only way to interpret the influence of minor phases on solar cell performance. As another alternative, the band offset might also be used to understand the effect of the minor phases in CZTSe on solar cell efficiency [66]. Fig. 2.4 shows the possible band alignments of secondary phase in CZTSe. In here, we will discuss in detail as below;

- If the secondary phase has a higher valance band maximum VBM and lower conduction band minimum CBM than that of CZTSe absorber, minor phase will act as a sink for both charge carriers in CZTSe (majority and minority carriers). Therefore, the charge separation will be hindered due to the facilitation of carrier recombination. Then, this leads to a reduction in cell performance [66]. Fig 2.4a shows the case discussed.

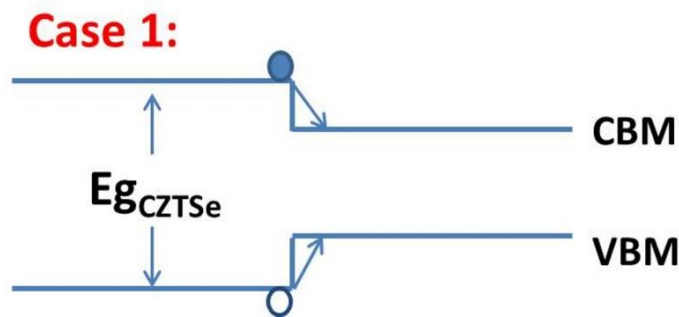


Fig 2.4 a) Band alignments in the case of smaller band gap of secondary phase in CZTSe absorber layer

- If the secondary phase has a lower valance band maximum VBM and higher conduction band minimum CBM than that's of CZTSe absorber, the band offset will become a barrier for both charge carriers in CZTSe due to the higher band gap of secondary phase. This leads to lower conductivity, but no improvement in recombination rate in CZTSe absorber [66]. Fig 2.4b represents the higher band gap of secondary phase than that of CZTSe.

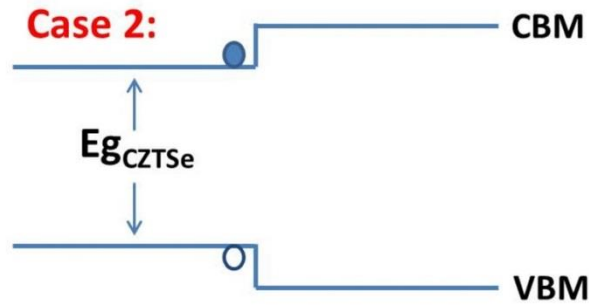


Fig 2.4 b) Band alignments in the case of larger band gap of secondary phase in CZTSe absorber layer

- If valance band maximum (VBM) and conduction band minimum (CBM) of secondary phases higher or lower than that of CZTSe as seen in Fig 2.4 c and d, respectively, the secondary phases acts as a sink for only one type of carrier and then, the carrier recombination will not be promoted [66].

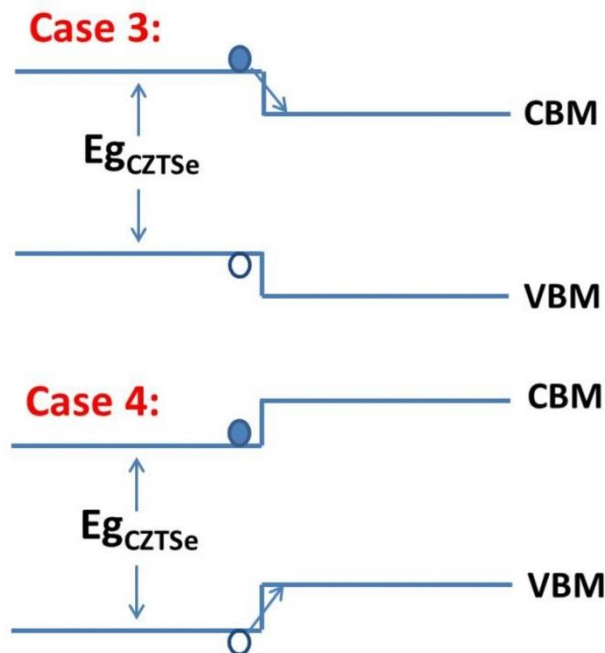


Fig 2.4 c) Band alignments in the case of lower CBM secondary phase in CZTSe absorber layer, d) higher VBM and CBM of secondary phase in CZTSe, respectively. (Fig. 2.4 sketched based on Ref. 66)

The possible minor phases and the impacts on the solar cells can be summarized in Table 2.2.

Table 2.2 Summary of the minor phases in CZTSe material with the electronic properties, impact on the solar cells and chemical etching solution to remove the minor phases

Minor Phases	Band Gap (eV)	Electrical properties	Possible composition	Impact on solar cell performance	Etching method
CuSe ₂	1.2-2.0	p-type	Cu-rich	causes short circuit	KCN
SnSe ₂	0.96-1.03	n-type	unlikely to occur, volatile	reduces V _{oc}	(NH ₄) ₂ S, (NH ₄)OH
ZnSe	~2.7	insulator	Zn-rich	decrease J _{sc} , increase series resistance	HCl, MnO ₄ /H ₂ SO ₄ + Na ₂ S
Cu ₂ SnSe ₃	0.5-0.9	p-type	Cu-rich Zn-poor	reduces V _{oc} , increases recombination rate	Br ₂ -MeOH

As a conclusion, when the secondary phases are present in the back region or bulk, completely avoiding the detrimental effect of these minor phases is not possible. It can be controlled by choosing ideal conditions such as precursors, composition, process parameters, post-deposition process, etc. It is also essential to detect these minor phases to optimize the fabrication process and to improve the solar cell efficiency. In next section, investigation of the minor phases in CZTSe thin film will be discussed.

2.4 Detection of secondary phases in Cu₂ZnSnSe₄ thin films

The formation of pure phase CZTSe thin films is difficult due to the narrow phase stoichiometry of CZTSe. Therefore, the coexistence of the secondary phases is more likely. The performance of the CZTSe solar cell suffers from the coexistence of these unwanted minor phases. As the matter of the fact, it is essential to detect these phases to optimize the solar cell performance. The common used laboratory tools are X-ray Diffraction (XRD) and Raman spectroscopy, to identify

the present phases in CZTSe thin films. However, they both have handicaps to detect the minor phases in CZTSe thin film. In literature, there are numbers of reports which show why XRD and Raman spectroscopy are insufficient tool to identify the secondary phases in CZTSe thin film [22,57,67-69]. It can be summarized that the crystal structures of ZnSe, CTSe, and CZTSe are similar, therefore, it is difficult to distinguish these phases from each other by XRD analysis [70-71], and Raman spectroscopy is a surface sensitive technique, therefore, acquiring signals for the bulk will be difficult. Additionally, a proper probing wavelength which provides resonant Raman scattering can be required to enhance the Raman signal and to identify specific phase (e.g. ZnSe and ZnS) [57,67,72,73]. In this thesis, we suggest an alternative tool which is SE to identify the secondary phases in CZTSe thin film and that will be discussed in Chapter 3 in detail.



Chapter 3

Spectroscopic Ellipsometry

3.1 Spectroscopic Ellipsometry (SE)

SE is an optical technique that measures the reflection (or transmission) from samples [74] and is based on the polarization properties of light. The name of ellipsometry comes from the elliptically polarized light. SE has been widely used in many application areas, such as chemistry, physics, biology, optical coating, data storage, etc. [74]. It can be also performed on SC material to measure the film thickness, surface roughness, substrate, and also to determine the optical constants, and interband structure, etc. [17,56,73-75].

SE is an indirect characterization method, and it has a few restrictions, like, surface roughness has to be small, and the measurement has to be performed at an oblique incidence. On the other hand, the advantages of the tool eclipse these restrictions. Because it is a non-destructive, fast, easily applicable technique and the precision of the measurement is quite high. In this chapter, we will focus on the application of SE on SC material and provide an overview of the measurement technique of SE and the data analysis procedures will be provided.

3.1.1 Polarized Light

Light is an electromagnetic radiation with a specific range of electromagnetic spectrum. When the light travels without any specific orientation or phase, i.e., randomly, the resulting light describes as unpolarized light. However, we are interested in polarized light which is required to perform SE measurement. It can be classified as linear polarized light, circular polarized light and elliptically polarized light.

Linear polarized light: An electromagnetic wave which is oriented in a defined plane is named to be linearly polarized light. Fig. 3.1.illustrates the transverse electric fields wave is accompanied by a magnetic field wave.

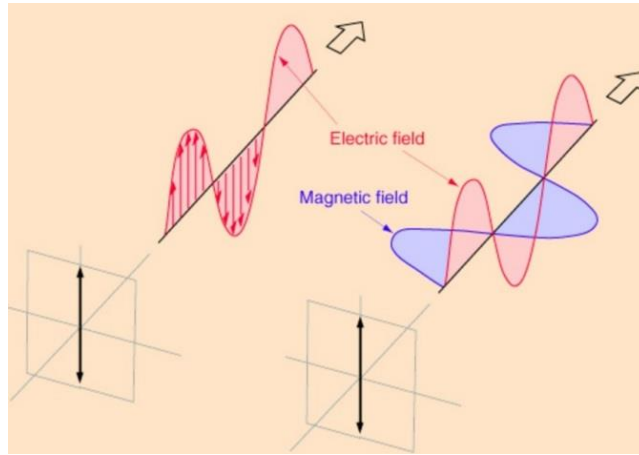


Fig. 3.1 Linear polarized light⁷⁶

Circular polarized light: If two combined orthogonal waves (which are linearly polarized) are out of phase by 90° but equal in amplitude, the resulting light is circularly polarized light shown in Fig. 3.2

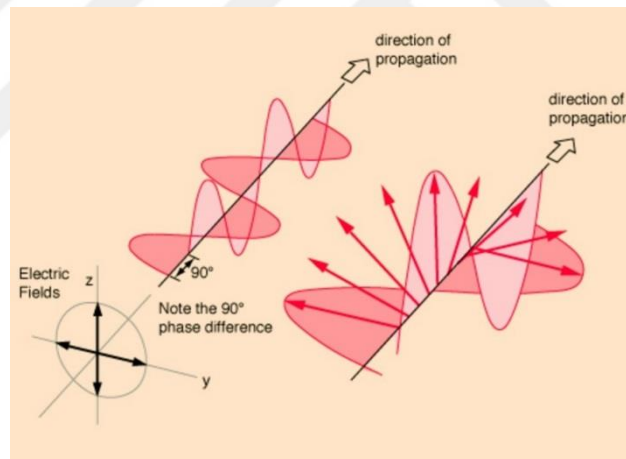


Fig. 3.2 Circular polarized light⁷⁶

Elliptical polarized light: If two orthogonal waves (which are linearly polarized) are combined which have arbitrary amplitude and phase, the resulting light is elliptically polarized light. Elliptically polarized light is illustrated in Fig. 3.3.

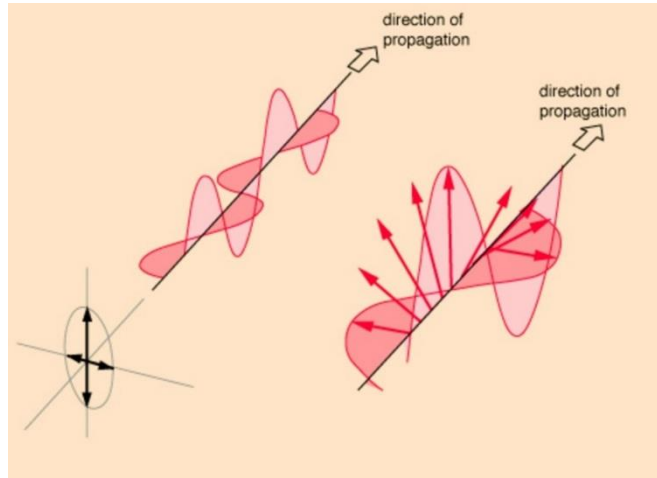


Fig. 3.3 Elliptical polarized light⁷⁶

Unpolarized light from the source is sent through a polarizer. Then, the polarizer lets the light pass through in a preferred electric field orientation. Thus, light becomes linearly polarized light. Linearly polarized light hits the sample surface and reflects. After reflection, the linear polarized light becomes elliptically polarized light due to the change in s- and p- polarizations. Then, the light arrives to the rotating analyzer and a detector detects the light intensity which passes through the analyzer. The detector converts light into electronic signal to obtain the reflected polarization. The instruments for a typical SE illustrates in Fig. 3.4.

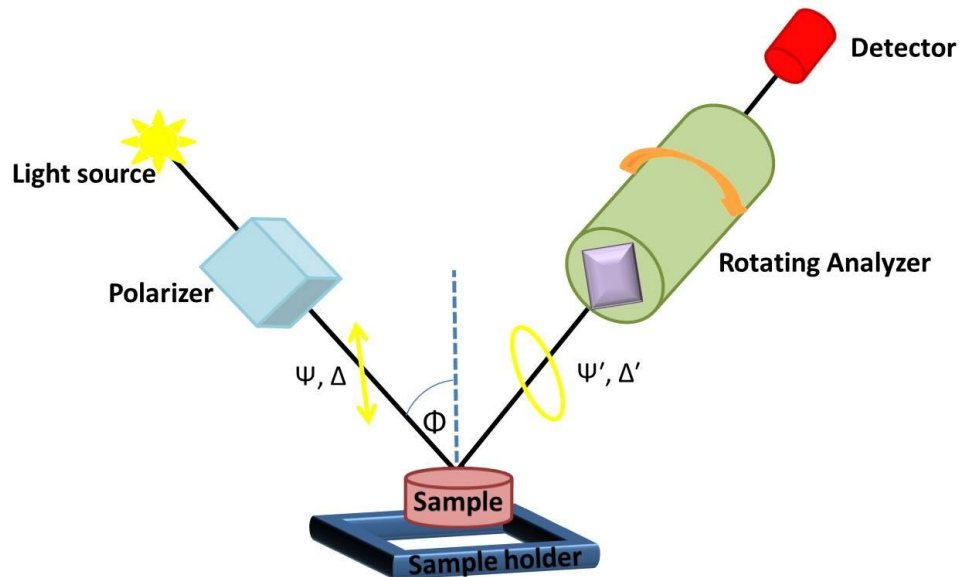


Fig. 3.4 Typical spectroscopic ellipsometry apparatus

It measures how s- and p- components of polarized light changes upon reflection or transmission through the sample [74]. The change in polarization of the ellipsometry measurement is described as in Eq. 1.

$$\rho = \tan(\Psi) e^{i\Delta}$$

The measurement parameters are Psi- Ψ and Delta- Δ , which represent the amplitude ratio and phase difference, respectively. The conversion of these values into optical parameters can only be done directly for very simple cases, i.e., the sample has to be infinitely thick, homogenous and isotropic. Otherwise, an optical model has to be constructed to make the data analysis. The constructed optical model is used to calculate the predicted response of Fresnel's equations which describe the material features [74]. Usually, all optical constants of analyzed material are present in SE database. Yet, for some materials such as CZTSe, MoSe₂, optical data does not exist in the SE database. In such a case, oscillator functions must be used to generate the dielectric function of examined material. This will be discussed in Section 3.2 in detail. The flowchart for data analysis of SE is illustrated in Fig. 3.5.

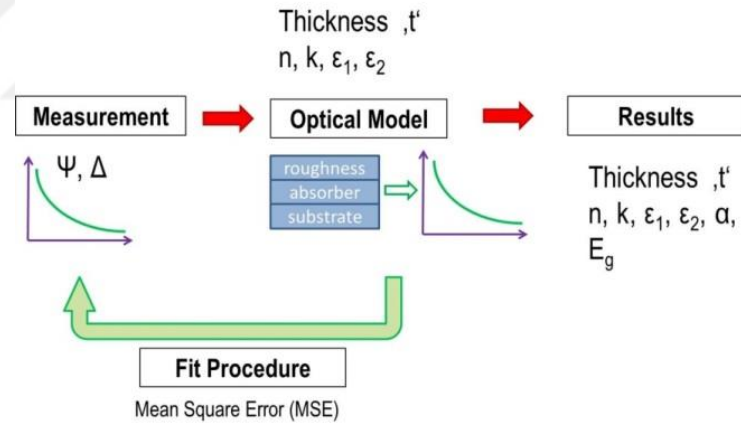


Fig. 3.5 The flowchart of SE data analysis

For the data analysis, the modeled optical data (theoretical data) and experimental data are compared to each other as a part of fitting procedure, to obtain the results including film thickness, optical constants, etc. To judge how good the comparison between these two data sets, an estimator is used such as Mean Square Error (MSE). The comparison in between experimental and theoretical data continues until reach the best match between these two data sets, i.e., the lowest value of MSE. Then, the thickness of the layers and optical constants can be extracted as shown in Fig. 3.5. However, it should be noted that the starting point of the thicknesses of layers for the fit procedure is important. This is because there are multiple 'local minima' and if the regression algorithm mistakenly falls into local minima, the fitting procedure

cannot be achieved properly. Therefore, to increase the reliability of the data analysis, different values of thicknesses have to be tried in order to find the global minimum which gives the correct thickness value, and also the lowest MSE value. Further, it is easy to distinguish the global minimum by comparing the results by eye for the local minima as seen in Fig. 3.6. Fig. 3.6 shows the MSE versus film thickness by addressing the local minima and global minimum [77]. The determination of film thickness will be discussed in Section 3.1.3.

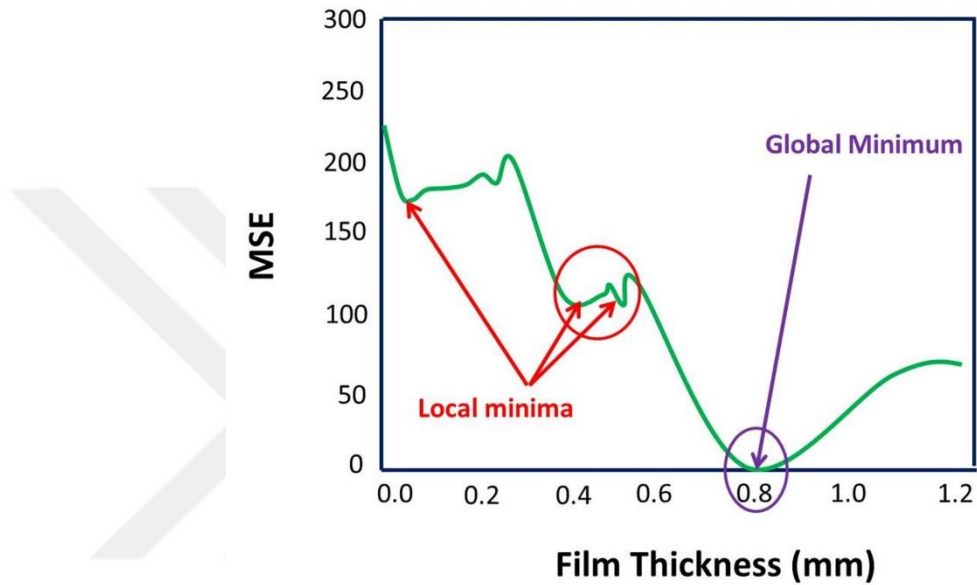


Fig. 3.6 MSE versus film thickness

3.1.2 Surface Roughness

The real surface metrology is always complex. Therefore, scientists have widely studied on the surface geometry with different techniques [78-80]. The asperity of surface geometry is consists of roughness, waviness, error of form and flaw [81]. Surface characteristic is illustrated in Fig. 3.8.

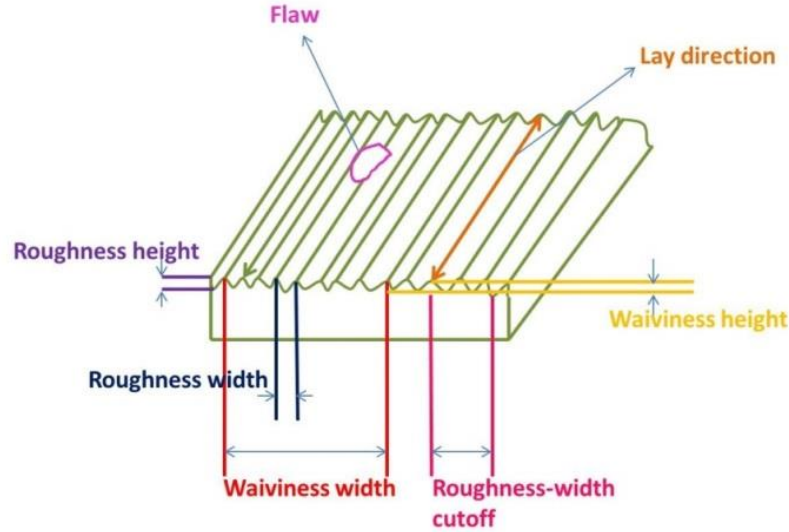


Fig. 3.8 Surface geometry

In this section, we will discuss SE. It is also used for the extraction of the surface roughness as well as the film thickness. However, SE is not preferred in case of a rough surface, since rough surface leads to a reduction in the reflected light intensity. Besides, if the length scale of the surface roughness exceeds 30% of the measurement wavelength, the error significantly increases [74]. Because the scattering will be dominant and the reflection will be negligible due to the rough surface, therefore, the surface roughness will not be represented anymore by Effective Medium Approximation (EMA). To reduce the surface roughness, the sample might be etched either mechanically or chemically. However, even if the etching process is done and the surface might be seen smooth by the naked eye, the surface roughness will never be zero at the microscopic scale. Hence, it is necessary to consider a surface roughness layer in constructed optical model for data analysis. Typically, the surface roughness consists of 50% void and 50% top layer of the material according to EMA [82,83]. EMA is a kind of analytical or theoretical modeling which describes the macroscopic properties of composite materials [82-84]. It will be discussed in subsection 3.1.2.1 in detail.

3.1.2.1 Effective Medium Approximation (EMA)

An EMA layer is often used to simulate the surface roughness and interfacial-roughness. It can also be used to simulate the volume fractions of the constituent materials and their physical geometry [82,83]. EMA layer allows us to combine the optical constants of two or three different materials together, provides the volume fractions of the constituents materials and the physical geometry [77]. The most common used EMA is Bruggeman and Maxwell-Garnett EMA layers. Bruggeman EMA layer is symmetric with respect to all medium components and can be used

under the conditions when the volume fraction is not very small. In contrast, Maxwell-Garnett EMA layer is not applicable when the volume fractions are comparable which is valid for small particles within the host material [85].

3.1.3 Film Thickness

Ellipsometry is usually used to measure the film thickness of a substrate [77,86]. When the light reflects from and passes through the thin film, the interference occurs due to the superposing of waves. Then, the film thickness is determined by interference. Interference can be either constructive (the movement of two interfering waves in the same direction) or destructive (the movement of two interfering waves in the opposite direction). The measured parameter Δ is sensitive to phase differences and it can be used to judge how reliable the extracted film thickness is. Therefore, SE is a preferred technique to assess the film thickness. However, the capability of the method to measure the thickness of a thin film is ranging from sub-nanometers to a few microns. [77]. Therefore, it is necessary to apply other techniques to extract the film thickness if the examined film is thicker, like tens of microns.

A simplified model for reflection and transmission as a refracted light at the interface of two different materials is illustrated in Fig. 3.7.

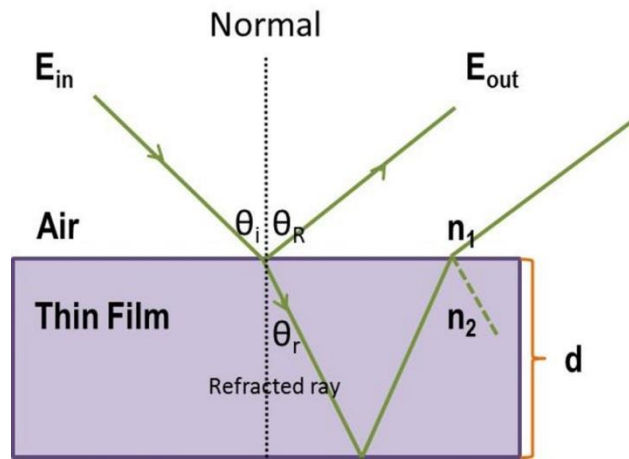


Fig. 3.7 Reflection and Refraction of light in a thin film

Light incident upon a sample surface will commonly reflect from and transmit as a refracted ray through the sample surface. To reflect from a surface, there are certain laws which called as ‘the law of reflection’ [87] as below;

- The incident ray, the reflected ray and the normal lie in the same plane.

- The angle of reflection is equal to the angle of incidence: $\theta_i = \theta_r$

However, the remaining part of the ray is refracted and travels through the second material (thin film), this is called ‘the refracted ray’ [87], and the direction of the refracted ray is known as the refracted angle θ_r . And, of course, there are requirements for the refraction as below;

- The incident ray, the refracted ray and the normal all lie in the same plane.
- The angle of incidence and the angle of the refraction are related by Snell’s Law:

$$\frac{\sin \theta_i}{\sin \theta_r} = \frac{n_2}{n_1}$$

where n_1 and n_2 are refractive indices for two different materials.

3.1.4 Optical Constants

SE allows a direct measurement of the refractive index n and extinction coefficient k , referred as optical constants. The refractive index describes how light propagates through the medium and is expressed by

$$n = c/v$$

where c is the speed of light and v is the phase velocity of light in the medium. The extinction coefficient is related to how fast light vanished in a material. The optical constants are usually defined by complex numbers such as complex refractive index or complex dielectric constants. The reason of expressing the optical constants with complex numbers is due to the attenuation of the light in the medium.

The complex refractive index is defined by $N = n - ik$. Extinction coefficient is related to the absorption coefficient α , $\alpha = 4\pi k/\lambda$ where λ is the wavelength.

The relation between complex refractive index and the complex dielectric constant is as below;

$$\varepsilon = N^2$$

The dielectric constant (permittivity) is defined as the magnitude of the polarization generated within a dielectric. The complex dielectric constant is expressed by $\varepsilon = \varepsilon_1 + i\varepsilon_2$, where ε_1 is the real component of the complex dielectric constants and ε_2 is the imaginary part of the complex dielectric constant and described as the polarization response of a material when an electric field is applied. If the ε_2 is known of the material, ε_1 can be calculated based on Kramers-Kronig relation that is a mathematical expression to describe any complex function.

As discussed above, optical constants can be derived from SE data analysis as well as the other physical properties of the material including film thickness and surface roughness.

3.2 Oscillators

If the analyzed material does not exist as a reference in the SE WVASE32 software, the user can use a tool in SE WVASE32 software to generate the oscillators in order to determine the dielectric function of the examined material. This tool also allows us to select various types of oscillator functions, to simplify modeling the material optical constant. There are different oscillators to parameterize the optical constants of different materials in the WVASE32 library. These are some of the oscillators in WVASE library: Cauchy oscillators, Lorentz oscillators, Harmonic oscillators, PSEMI oscillators, etc. Cauchy oscillators are used for transparent material, Lorentz Oscillators are for semiconductors and metals, Harmonic oscillators are typical for Harmonic oscillator model and PSEMI oscillators are used to parameterize semiconductor oscillator model for modeling the crystalline semiconductors dielectric functions [77].

In this thesis, all extracted optical constants from SE data analysis for CZTSe and MoSe₂ samples were modeled by using oscillation function consisting of PSEMI oscillators. The reasons for selecting PSEMI oscillators are they are useful to fit dielectric functions of a SC material and easy to shape due to the flexibility of the oscillator functions. In next section, PSEMI oscillators will be discussed in detail.

3.2.1 PSEMI Oscillators

There are five types of PSEMI oscillators in SE WVASE32 library, called as *Psemi-M0*, *Psemi-M1*, *Psemi-M2*, *Psemi-M3*, *Psemi-Tri*, respectively. All these oscillators are based on Herzinger-Johs Parameterized Semiconductor Oscillator functions [77]. They were developed at J. A. Woollam Co., Inc. by Craig Herzinger and Blaine Johs, intended for analyzing compound SCs [77]. These functions are very useful to fit the dielectrics and both direct and indirect band gap of SC materials [77]. Therefore, PSEMI oscillator was preferred to generate the optical constants from the designed optical model. Another reason is that the oscillator function shapes are very flexible and any dielectric functions can be modeled by using them.

Each oscillator function has 12 parameters. However, only 7 of them are active to fit the optical constants of the semiconductor material and, the rest of parameters are fixed. Thus, each oscillator function has a distinctive shape. Table 3.1 summarizes the variable and fixed parameters for each PSEMI oscillators and the function parameters [77] are below;

A, E & B: Amplitude, Broadening & Center Energy.

WL & WR: Endpoint positions relative to the E. They set the width of the oscillators left and right sides, respectively.

PL & PR: Horizontal positions of the left and right control points, relative to the center energy and the endpoints.

AL & AR: Relative magnitude of the left and the right sides of the control points, respectively.

O2L & O2R: Coefficients for the 2nd order terms in the polynomials on the left and the right sides of the *Psemi-M0* and *Psemi-M3* oscillators. Add additional flexibility the function.



Table 3.1 Psemi Oscillators with variable and fixed parameters⁷⁷

Psemi.mat parameters	Energy	Amp	Br	Left/Right Boundaries set by E of connecting oscillators		Left Mid		Right Mid		Left 2 nd order	Right 2 nd order	Discontinuity
						Mid Pos	Mid Amp	Mid Pos	Mid Amp			
Equivalent Genosc.mat parameters	E	A	B	WL	WR	PL	AL	PR	AR	O2L	O2R	Not accessible in Genosc
<i>PSEMI-M0</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>0</i>	<i>Active</i>	<i>0.5</i>	<i>0.5</i>	<i>Active</i>	<i>Active</i>	<i>0</i>	<i>Active</i>	<i>0</i>
<i>PSEMI-M1</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>0.75</i>	<i>Active</i>	<i>0.5</i>	<i>Active</i>	<i>1</i>	<i>0</i>	<i>0</i>
<i>PSEMI-M2</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>0.5</i>	<i>Active</i>	<i>0.75</i>	<i>Active</i>	<i>0</i>	<i>1</i>	<i>0</i>
<i>PSEMI-M3</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>0</i>	<i>Active</i>	<i>Active</i>	<i>0.5</i>	<i>0.5</i>	<i>Active</i>	<i>0</i>	<i>0</i>
<i>PSEMI-Tri</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>Active</i>	<i>0.5</i>	<i>Active</i>	<i>0.5</i>	<i>Active</i>	<i>0</i>	<i>0</i>	<i>0</i>

3.3 Semiconductors

SE can be performed on SC material to evaluate the film thickness, optical constants and optical transitions, etc. Typically, SC material is characterized at 70° - 80° incidence angle and the Brewster angle for CZTS and CZTSe compound SC material is 67° and 69° , respectively. Note that it is important to characterize the SC material at Brewster angle (oblique angle) since the ellipsometry measurement become impossible at normal incidence due to the indistinctness of the s- and p- polarizations [74]. The optical constants of SC material have been widely studied in the literature [9,17,56,73,75,84,89-92]. Although there has been quite number of studies on analysis of some SC materials by SE, still there is not enough optical data for some SC materials such as CZTSe, CZTS, CZTSSe compound SC. Further, if the dielectric constant of the material is not known, the data analysis becomes complicated due to the complicated structures of the dielectric function of the material [74]. In such a case, the oscillator function has to be used to extract the optical constants of the material for the SE data analysis as discussed in section 3.2. The thickness of the SC material can be determined in the case of knowing the dielectric constants and vice versa. SE can be performed to determine the film thickness, dielectric function as well as optical transitions in SC material. This section will provide an overview of optical transitions in SC material.

3.3.1 Optical Transitions in Semiconductors

In SC material, conduction bands CB and valance bands VM are separated by certain energy which is called band gap. If the top of the valance band VB and the bottom of the conduction band CB are placed at a common wave vector, k , the transition is called direct transition. But if the valence band maximum and conduction band minimum have different k values, the transition is called indirect transitions [93]. Both transition types are illustrated in Fig. 3.8.

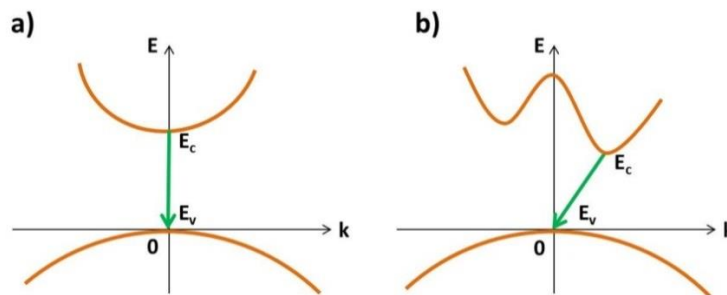


Fig. 3.8 Optical transitions a) direct transition, b) indirect transition

The absorption coefficient is proportional to the band gap of the material. The relation between absorption coefficient and the band gap of the material is as below,

$$\alpha(h\nu) = A(h\nu - E_g)^{0.5} \text{ (Direct transition)}$$

$$\alpha(h\nu) = A(h\nu - E_g)^2 \text{ (Indirect transition)}$$

where A is constant. E_g can be extracted from Tauc plot of the linear region of $\alpha(h\nu)^2$ versus $(h\nu)$ or $\alpha(h\nu)^{0.5}$ versus $(h\nu)$, depending on the transition type. The absorption coefficient α can be calculated by using the expression of $= \frac{4\pi k}{\lambda}$, k is the extinction coefficient, can be extracted by SE measurement. The relation between complex refractive index and the complex dielectric function is given in Section 3.1.4.

Persson [9] reported the electronic band structure of CZTSe SC material which is given in Fig 3.9. The first transition in CZTSe material is a direct transition and further transitions are not well known due to the flat dispersion of the bottom of the CB and the top of the VB. As seen in Fig. 3.9, the lowest CB is a lone band due to the contribution of Sn to the electronic band structure.

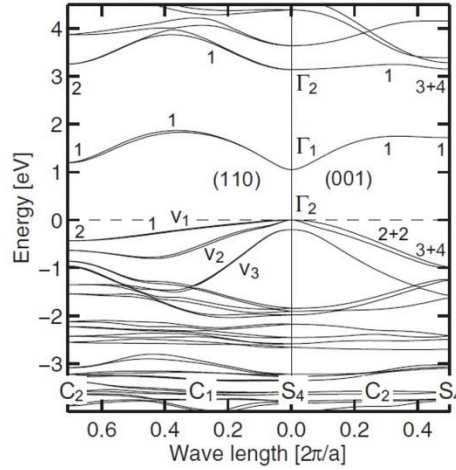


Fig. 3.9 Electronic band structure of $\text{Cu}_2\text{ZnSnSe}_4$ ⁹

The band structure of a SC is usually studied theoretically. However, the dielectric function of a SC material is related to its electronic band structure and the features observed in the imaginary part of the dielectric constant ϵ_2 are linked to interband transitions in the material, i.e., critical

points CPs. Therefore, the band structure of a SC can be also studied experimentally by SE. The behavior of the dielectric function of a near CP is expressed by [94,95];

$$\varepsilon(E) = Ae^{i\Phi}(E - E_g + i\gamma)^n$$

A is the amplitude, Φ phase angle, E_g the threshold energy, γ the broadening. The exponent n can be $-1/2$, 0, $1/2$ for one dimensional 1D, two dimensional 2D and three dimensional 3D CPs, respectively. CP parameters of electronic transitions can be determined by a fitting procedure of the numerically calculated second derivative of complex dielectric function $\frac{d^2\langle\varepsilon\rangle}{dE^2}$. The optical transitions in CZTSe are detailed in Chapter 6.



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Chapter 4

Detection of a MoSe₂ secondary phase layer in CZTSe by spectroscopic ellipsometry

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My contribution to the article

- Idea and the conception of the experiments
- Spectroscopic ellipsometry measurement including optical modeling, fitting and interpretation of the results
- Raman spectroscopy measurement including the data analysis and the interpretation of the results.
- SEM cross-section measurement including interpretation of the results
- Preparation of the Br₂-MeOH etching solution with the help from Mathias Macke
- Preparation of the samples for the measurements including lift-off process and etching process
- Manuscript design and figure preparation
- Manuscript writing with the input from the co-authors
- Discussion with the referees



Detection of a MoSe₂ secondary phase layer in CZTSe by spectroscopic ellipsometry

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We demonstrate the application of Spectroscopic Ellipsometry (SE) for identification of secondary phase MoSe₂ in polycrystalline Cu₂ZnSnSe₄ (CZTSe) samples. A MoSe₂ reference sample was analyzed, and its optical constants (ϵ_1 and ϵ_2) were extracted by SE analysis. This dataset was implemented into an optical model for analyzing SE data from a glass/Mo/CZTSe sample containing MoSe₂ at the back side of the absorber. We present results on the n and k values of CZTSe and show the extraction of the thickness of the secondary phase MoSe₂ layer. Raman spectroscopy and scanning electron microscopy were applied to confirm the SE results. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4935258>]

I. INTRODUCTION

Recently, the compound semiconductor material Cu₂ZnSn(S,Se)₄ has been investigated intensively as it is a promising candidate for application in thin film solar cell devices. The compound contains earth abundant metals and is expected to allow for low production costs of solar cell devices. Cu₂ZnSn(S,Se)₄ has a direct band gap ranging from 1 eV for Cu₂ZnSnSe₄ (CZTSe) to 1.5 eV for Cu₂ZnSnS₄ (CZTS),^{1–3} and a high absorption coefficient of 10^{-4} cm^{-1} at energies slightly above the band gap. Besides these properties, the achieved increase of record efficiencies makes CZTSe a good candidate for solar cell application.⁴ It is known that the formation of secondary phases can limit the performance of the solar cell device.^{5–8} Therefore, a quick and non-destructive method for identification of these phases is of high importance.

Spectroscopic ellipsometry (SE) is a fast and non-destructive technique to obtain optical and structural properties of materials such as dielectric functions, refractive index, layer thickness, and roughness, providing fundamental information about the characteristics of a layer and its interfaces.

Recently, several SE studies on CZTS/Se were published, investigating fundamental optical properties of Cu₂ZnSnSe₄ such as absorption coefficient, complex dielectric constant, and/or band gap energy.^{9–12} These studies either investigated the properties of CZTS/Se grown on other substrates than the usually used Molybdenum or the impact of the Mo substrate on the back side of the absorber was neglected, which occurs to be a critical issue for CZTS/Se processing.

II. SPECTRAL ELLIPSOMETRY

In this study, we shed light on this hitherto neglected but critical aspect and focus on the investigation of this interface

region and the identification of the secondary phase molybdenum diselenide (MoSe₂) by SE. For many growth procedures, this secondary phase appears in the interface region of the Mo back contact and the CZTSe layer. We show that the presence and amount of MoSe₂ in a Mo/MoSe₂/CZTSe structure can be identified and quantified by an extended analysis of the SE results if this phase is present as a layer. This further allows to reduce the effect of the MoSe₂ layer on the obtained dielectric functions for CZTSe and thus to get more reliable results for optical constants of the pure CZTSe bulk.

SE is a powerful tool to analyze fundamental optical properties, i.e., complex dielectric functions of the material. The measurement in SE consists of detecting the signal height and the change in polarization of the reflected light which are expressed as Psi (Ψ) and Delta (Δ), respectively.^{13,14} These two measured parameters cannot be converted to optical properties directly if the material does not consist of a fully isotropic, homogenous, and infinitely thick ideal structure. Therefore, it is necessary to build an optical model to analyze the recorded data and to extract the requested optical parameters. For this purpose, the optical model parameters are being iteratively modified to obtain an agreement between experimental and modeling results.¹⁴ Depending on the modeled sample geometry and modeled optical dielectric functions, the parameters Ψ and Δ can be calculated. For evaluation of the SE results, these theoretical values are compared with the experimental Ψ and Δ data. The modeling parameters are subsequently varied until the best fit between calculated and experimental data is found.

The basic relationship between Ψ , Δ and the optical constants is given by

$$\tan(\Psi) e^{i\Delta} = R_p/R_s, \quad (1)$$

where R_p and R_s are the Fresnel reflection coefficients for the p- and s-polarized light, respectively.¹⁴

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III. EXPERIMENTAL

In this study, we show results for two different CZTSe samples (referred to as sample A and sample B) and a MoSe₂ reference sample. The MoSe₂ reference sample was obtained from a sample from an industrial standard process after lift-off of the absorber layer followed by a bromine methanol etching. Details of the processing and the structure of the sample are described elsewhere.¹⁵ Homogeneity and phase purity of the MoSe₂ layer were confirmed by scanning electron microscopy (SEM), energy dispersive x-ray (EDX), XRD, and glow discharge optical emission spectroscopy. This reference sample was used to investigate the dielectric function of MoSe₂ to allow for its identification in CZTSe samples and its clear separation from the CZTSe layer in the optical modeling. Samples A and B were fabricated at the University of Luxembourg. Sample A was prepared by a sequential process with a co-evaporated precursor, which was, consequently, annealed in a Se-SnSe atmosphere.¹⁶ Sample B was prepared by a high temperature co-evaporation process.¹⁷ The compositions of the samples were Cu/(Zn + Sn) $\approx$ 0.8 and Zn/Sn $\approx$ 1.2 for sample A and Cu/(Zn + Sn) $\approx$ 0.9 and Zn/Sn $\approx$ 0.9 for sample B.

Due to the different processing routines, the resulting sample structure shows differences between samples A and B, especially in terms of formation of MoSe₂ between the absorber and the Mo back contact. Companion samples of the investigated specimen have achieved efficiencies of $\approx$ 5% and $\approx$ 6% for samples A and B, respectively.

For structural and optical investigations, which were performed at the University of Oldenburg, the CZTSe samples and MoSe₂ reference sample were etched with 0.02 M bromine methanol (Br₂-MeOH). This etching process was done in subsequent steps to reduce the effect of surface roughness and to remove potential secondary phases and oxides at the surface region in order to reduce possible artifacts in SE experiments, which would otherwise decrease the signal-noise-ratio of the measurements, the quality of the fits, and thus, influence the results for the optical constants. The potential secondary phases in this region include binary or ternary compounds, which are effectively removed by the etching procedure.¹⁸

The final durations for the etching of each sample were determined by an optimum signal-noise ratio, which was observed for 90 s, 30 s, and 15 s for sample A, sample B, and the MoSe₂ reference sample, respectively.

To analyze the Mo/MoSe₂/CZTSe interface region directly, an un-etched part of each sample was lifted off onto a microscopy glass slide by using super glue, allowing for a direct analysis of the absorber back side and the remaining substrate surface.

Spectroscopic ellipsometry was performed in a setup containing a rotating analyzer (J.A. Woollam Co, VASE) in the wavelength range from 240 nm to 1700 nm and at incidence angles of 65°, 70°, and 75°. Raman measurements were done at an excitation wavelength of 532 nm with 3 mW excitation laser power in a LabRAM Aramis from Horiba. SEM pictures were obtained in a FEI SEM/FIB-system.

IV. SE RESULTS AND MODELING

For a proper evaluation of the experimental results and to make unambiguous interpretations based on the measurements, a well-defined model of the different sample structures has to be created which includes all layers present, interfaces, surfaces and structural properties, and anomalies of the sample. Although the surface of the material may appear smooth on a first glance, it is rough at the microscopic scale. To account for the roughness, a layer consisting of 50% void and 50% top layer material according to the Bruggemann effective medium approximation (EMA)¹⁹ is added on top of the stack layer. Furthermore, an “interface layer” between absorber layer and molybdenum has to be considered to account for a non-ideal interface and possible secondary phases occurring at the back contact. Fig. 1 shows the basic optical model for SE analysis which is used for evaluation of the measurement data from SLG/Mo/CZTSe samples. The dielectric function of Mo was taken from the database of WVASE32 software.

The simplest case of an interface layer is an EMA intermix layer comprising the optical properties of the adjacent layers, i.e., CZTSe and Mo (referred to as model 1: Mo/Intermix/CZTSe). This intermix layer would roughly account for a non-ideal interface between two layers due to the interface roughness. As it is well known that MoSe₂ often occurs at the interface in Mo/CZTSe structures, the next step to build a more elaborate model is to replace this intermix layer by a defined MoSe₂ layer as an “interface layer” (referred to as model 2), for which we investigated a MoSe₂ reference sample. In the third model, we introduce EMA intermix layers between Mo and MoSe₂, and MoSe₂ and CZTSe to account for inhomogeneous layer thicknesses and non-ideal interfaces (referred to as model 3). Results for further optical models of higher complexity, including additional layers to account for further secondary phases, are underway.

Despite SE being measured for the whole spectral range for each sample, the fitting range was limited to exclude measurement artifacts in the fitting procedure. For sample A, we chose the energy range between 0.85 eV and 4.5 eV whereas for sample B, the energy range between 0.75 and 3 eV was chosen. Below 0.85 eV for sample A and above 3 eV for sample B, no useful data could be obtained even after multiple measurements on different sample positions due

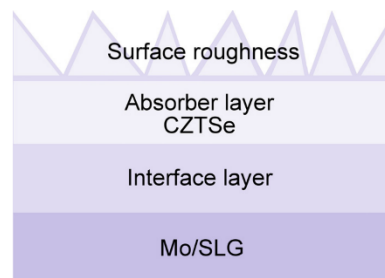


FIG. 1. Layer structure of the basic optical model for interpretation of ellipsometry data.

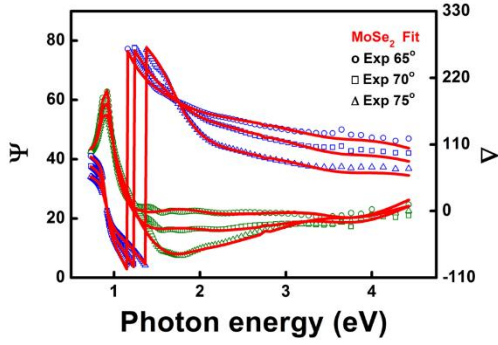


FIG. 2. Measured and fitted Ψ and Δ data for the MoSe_2 reference sample (green symbols: Ψ , blue symbols: Δ , and red solid lines: model fit).

to the signal noise and scattering. This effect can be explained by crystal disorder, inhomogeneities, or other artifacts at the back side of sample A and at the front side of sample B, as SE is sensitive to non-idealities at the back or the front side of the probed layer in the low or high energy regime, respectively. Essentially, it is not expected to see a significant effect of the secondary phase of MoSe_2 at the back side for high photon energies due to the absorption of these photons in the absorber. Therefore, an additional investigation of the low energy range at 0.85–1.5 eV for sample A and at 0.75–1.5 eV for sample B is preferable to understand the impact of the back contact and secondary phases in the interface region. Surprisingly, the scattered signal at high energies for sample B could not be improved by another etching step, indicating that the artifacts are not caused by oxides at the surface but rather by the properties of the absorber in the top region of the sample.

Fig. 2 shows Ψ and Δ data for the MoSe_2 reference sample at different incident angles and the fit of the evaluation model. The extracted complex dielectric functions for the MoSe_2 reference sample are shown in Fig. 3. The results are obtained for the energy range between 0.75 eV and 4.5 eV and are implemented into the optical models of samples A and B as mentioned above. There is a small spike visible at around 2.75 eV for ϵ_1 due to fitting artifacts. However, since the largest part of the photons at this energy is absorbed in the experiment in the CZTSe layer, the contribution of the

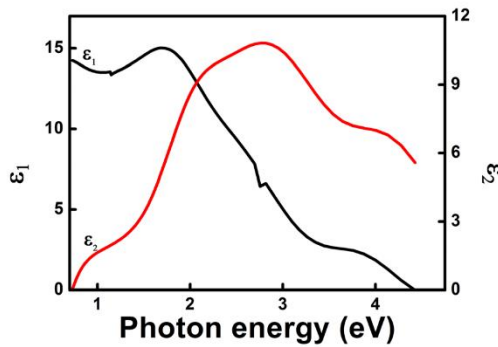


FIG. 3. ϵ_1 and ϵ_2 of MoSe_2 reference sample as extracted from SE.

back contact in this energy range can be neglected for the further discussion.

In Fig. 4, we show experimental SE data (Ψ and Δ) for different incident angles versus photon energy. The experimental data are fitted by application of optical model 1 (red solid lines). The data for samples A and B in the energy ranges between 0.85 and 4.5 eV and between 0.75 and 3 eV are shown, respectively. The thicknesses of the layers, which also relate to the amount of the occurring secondary phase MoSe_2 , are evaluated by different optical models and are shown in Table I.

Applying the three optical models to both samples reveals the layer thicknesses as shown in Table I. The MSE (Mean Square Error) is shown as well to provide a measure for the quality of each fit. All fit parameters are rounded to one digit after the comma as smaller variations show almost no impact on the overall fit quality.

Regarding sample A, by modeling a MoSe_2 layer instead of an intermix layer, the fit improves especially in the low-energy range. In general, the MSE is increased for the 0.85–1.5 eV energy range for all applied models. This can be explained by a worse quality of the CZTSe crystal or other artifacts like inhomogeneities in the vicinity of the back contact. However, according to these results, we can state that the best optical model includes a defined MoSe_2 layer with a thickness of around 210 nm. SE measurements at different positions on sample A reveal that this thickness varies between 150 nm and 220 nm. These results are confirmed by

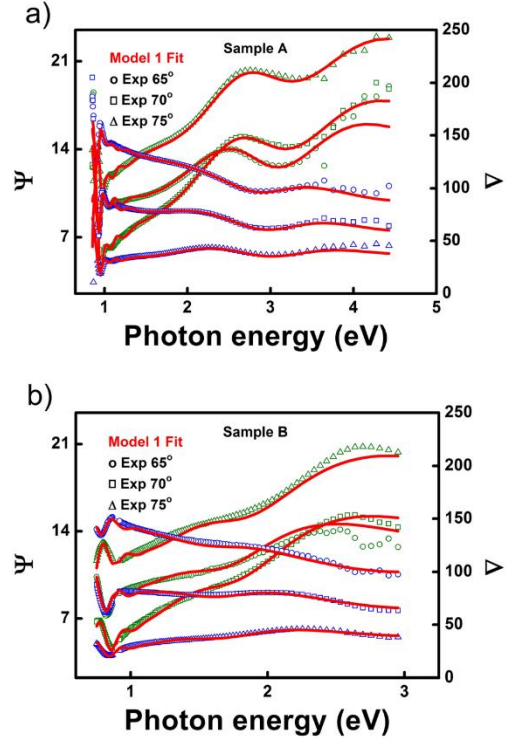


FIG. 4. Measured and fitted Ψ and Δ (green symbols: Ψ , blue symbols: Δ , and red solid lines: fit with optical model 1).

TABLE I. Fitting results for the three models including the thicknesses of the interface layer, CZTSe absorber, and EMA surface roughness layer as well as the MSE (Mean Square Error). The fits are shown for samples A and B for different photon energy fit ranges. The configuration of the interface layer depends on the optical model: model 1: EMA intermix layer, model 2: MoSe_2 , and model 3: Intermix/ MoSe_2 /Intermix.

Sample and fit range	Interface layer thickness (nm)	CZTSe (nm)	Roughness (nm)	MSE
Sample A (0.85–4.5 eV)				
Model 1	267.2	1192.6	14.7	10.9
Model 2	209.4	1285.8	12.5	10.5
Model 3	1.6/205.4/0.0	1302.9	12.6	10.3
Sample A (0.85–1.5 eV)				
Model 1	270.7	1191.4	14.6	15.4
Model 2	211.2	1285.3	12.8	14.5
Model 3	2.5/205.3/2.6	1302.8	12.6	14.4
Sample B (0.75–3.0 eV)				
Model 1	9.2	1345.1	7.3	5.5
Model 2	0.0	1347.1	7.3	5.6
Model 3	8.5/0.0/8.1	1346.0	7.4	5.5
Sample B (0.75–1.5 eV)				
Model 1	17.8	1343.8	7.4	6.2
Model 2	0.0	1349.0	6.9	6.3
Model 3	14.4/0.1/4.4	1345.8	7.4	6.2

SEM cross sections which show a MoSe_2 layer with fluctuating thickness in the same range, exemplarily shown for one position in Fig. 5(a).

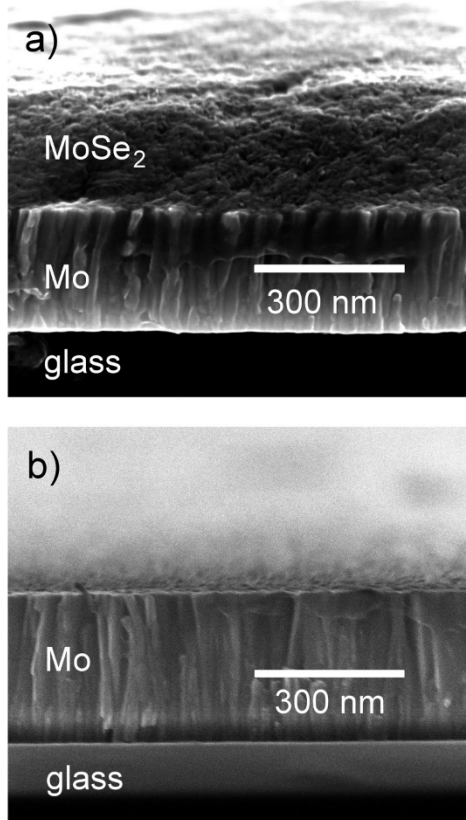


FIG. 5. SEM results obtained from remaining substrate part after absorber lift-off (a) for sample A and (b) for sample B.

The same optical models were applied to sample B but at different energy regions as mentioned above. The MSE is comparable for both energy ranges as shown in Table I. Hence, in contrast to the behavior of sample A, it can be concluded that the crystal quality at the back contact differs only slightly from the entire bulk. The fitting results of the second and third optical models give a MoSe_2 thickness of zero, and therefore, almost no change in the MSE between the different models. Only the low energy range fit for the third optical model may indicate a very thin MoSe_2 layer, with the thickness being in the range of the fitting error. Thus, the SE results for this sample show no solid indication for the existence of a closed MoSe_2 layer. However, the fit results show the intermix layers with small thicknesses, which add up to 10–20 nm in total for the entire interface region between Mo and CZTSe. This can be explained by interface roughness and/or the presence of a secondary phase (MoSe_2 or ZnSe inclusions which are discussed further below) which does not appear as a closed layer. Slightly different overall thicknesses for the “interface layer” are observed for the two fitted energy ranges. These can be explained by the different sensitivities of the fit for the back side of the sample depending on the used energy range, i.e., higher and lower sensitivities for 0.75–1.5 eV and 0.75–3.0 eV, respectively. For the low energy range fit, the optical models 1 and 3 show similar overall thicknesses of the interface layer. The visible slight discrepancy in the full energy range fit for sample B can be accordingly explained by the lower sensitivity at the back side of the sample for this fitting range.

In the SEM picture in Fig. 5(b), no MoSe_2 layer can be observed, indicating that—if present at all—the layer has a thickness below the resolution of the SEM setup, which is in the range of <10 nm. This result is in good agreement with the interpretations of the SE results. Note that the SEM cross sections were obtained from remaining substrates after absorber lift-off. A lift-off of MoSe_2 which would remain at

the back side of the absorber can be excluded by Raman results, see further below.

Fig. 6 shows the comparison of Ψ and Δ with the fit results of the three different optical models of each CZTSe sample (referred to as model 1, model 2, and model 3). While the fits of all three models overlap almost perfectly for sample B (Fig. 6(b)), we can see differences for the results for sample A. Here, the results for model 1 differs from the behavior of models 2 and 3, which show an almost identical behaviour. The deviation of model 1 from the experimental data and from models 2 and 3 is visible in the low energy regime which is mostly influenced by the modeling of the back contact interface, and it is the strongest in the region around 1100 nm.

In Fig. 7, we show experimental n and k values of CZTSe for each sample which were extracted with different optical models (a) in the energy range between 0.85 and 4.5 eV for sample A and (b) in the energy range between 0.75 and 3.0 eV for sample B.

For sample A, we observe a difference between the results for n and k for different optical models. While the results for models 2 and 3 are very similar, they show slight differences in peak shapes and positions compared with model 1. In analogy to the fits shown in Fig. 6, the results for

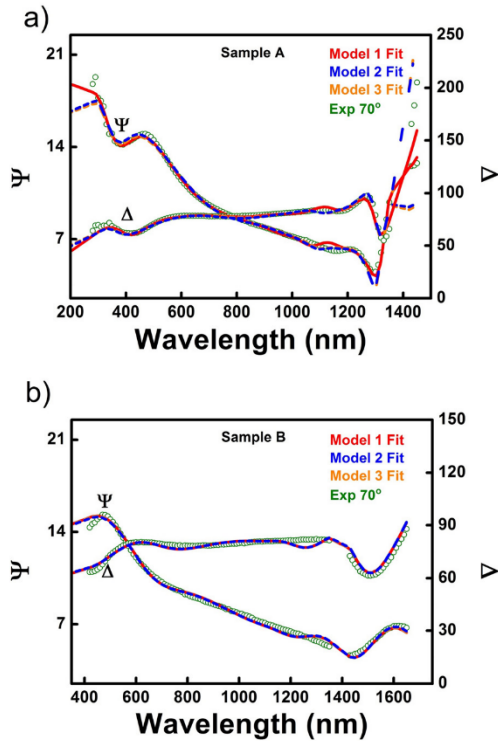


FIG. 6. Comparison of experimental and fitted Ψ and Δ for three optical models, for (a) sample A and (b) sample B (only incident angle of 70° shown). Green circles: experimental data, red solid line: model 1, blue dashed line: model 2, and orange dashed line: model 3 (lines do partially overlap).

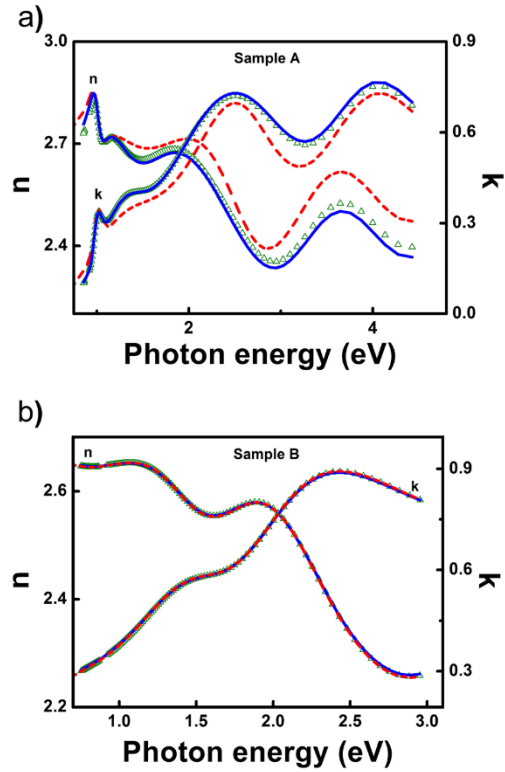


FIG. 7. Extracted n and k values of CZTSe determined by SE with different optical models, (a) sample A and (b) sample B; red dashed lines: model 1, blue solid lines: model 2, and green triangle symbols: model 3.

sample B (Fig. 7(b)) show no difference of n and k values for different optical models.

Our result shows similar k values but lower n values in comparison to the reported numbers by León *et al.*,²⁰ which can be explained by a different growth process and composition. Due to the different growth processes, a difference of the long range crystal order and grain sizes can be expected. Additionally, surface roughness (also influenced by grain boundary density) can alter n values. Differences in comparison to the results reported by Choi *et al.* can be explained by their application of the simplest case for an optical model for CZTSe/Mo, which neglects the interface region.¹¹ Furthermore, the minimum in absorption at around 3.2 eV matches the results published in Ref. 21 and can be explained by the presence of two band gaps in CZTSe absorbers as was predicted by the theoretical calculations.^{1,22}

Fig. 8 shows Raman measurements for samples A and B which were performed for the back and front sides of both CZTSe absorbers and the remaining SLG/Mo surfaces after absorber lift-off.

A. Raman results

The Raman results for sample A which were measured from the SLG/Mo substrate clearly confirm the presence of a secondary phase MoSe_2 layer at the Mo/CZTSe interface.

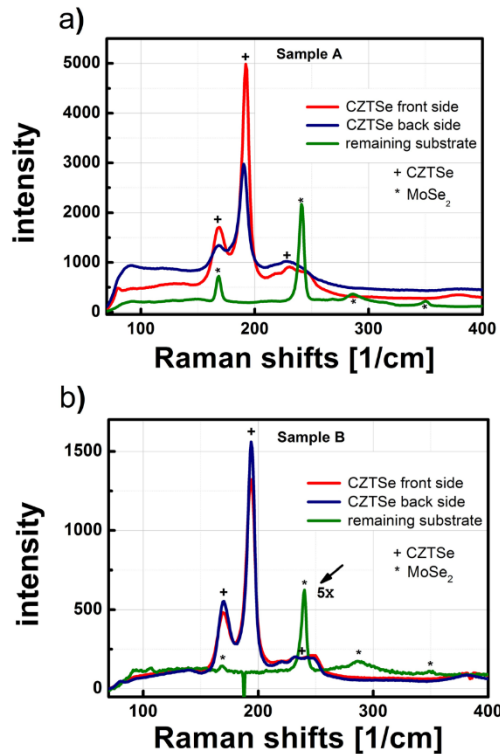


FIG. 8. Raman spectra (532nm excitation wavelength) for front and back sides of CZTSe absorber and remaining SLG/Mo substrate surface after absorber lift-off for sample A and sample B, respectively.

CZTSe fingerprints are observed for both the front and back side of the absorber with the known peaks around 170 cm^{-1} , 190 cm^{-1} , and 235 cm^{-1} as known from literature.^{5,23–26} Raman peaks for the remaining substrate show MoSe_2 fingerprints at around 169 cm^{-1} and 240 cm^{-1} which agrees well with numbers from literature.²⁷ The Raman peaks for the back side appear broadened when comparing with the spectrum for the front side of the absorber. Further, the intensity at the back side is lower than at the front side. The observed decrease in Raman intensity and the broadening of the peaks can be explained by low crystal quality and/or inhomogeneity in the back region of the absorber, as was already indicated by the SE results on the samples before lift-off.

Sample B (Fig. 8(b)) shows MoSe_2 peaks with very low signal intensity on the SLG/Mo surface; the spectrum is magnified by a factor of 5 for better observation. Additionally, CZTSe fingerprints on the front and back side of the absorber were detected. In this case, there is only a very slight difference in Raman peak shapes between back and front side of the absorber. We can interpret that the crystal quality of the back side is very similar to the front side of the absorber which is in accordance to the previously discussed SE results. Additional SEM measurements (not shown here) also reveal a few ZnSe inclusions at the back side for sample B. The comparison between the front and back side Raman spectra shows a slightly higher signal at the position of the ZnSe

peak at around $245\text{--}250\text{ cm}^{-1}$ for the back surface, which can preliminarily be interpreted as a confirmation of these ZnSe inclusions at the back side.^{5,23,26} The existence of a few ZnSe inclusions at the back side can cause a small influence on the measured SE signals in the low energy range. Therefore, the optimum optical model for sample B should include an intermix layer below the CZTSe layer to account for the possible secondary phase inclusions of MoSe_2 and ZnSe or other inhomogeneities etc., at the back interface, as already discussed in Section IV (see model 3).

V. CONCLUSION

Two CZTSe samples from different growth procedures on Mo coated soda lime glass and a MoSe_2 reference sample were investigated. Raman and SEM were performed to identify and characterize a layer of a MoSe_2 secondary phase by preparing the samples by a glue and lift off procedure. It was demonstrated that SE can be applied as a non-destructive technique to obtain the same information on SLG/Mo/CZTSe samples. We have shown that the choice of the optical model is critical for the obtained SE results such as thickness, imaginary part of complex dielectric function, refractive index, and extinction coefficients. The slight differences to results in literature can be explained by different growth procedures and compositions. The effect of composition on the optical constants is currently under investigation and will be published separately.

SE is a powerful tool to detect secondary phases such as MoSe_2 and to obtain its thickness as a non-destructive technique. The drawback of this technique is its inability to detect secondary phases if there is no closed layer. In such a case, additional methods are required to obtain the requested information. Further, the SE fitting results can be used as an indicator for crystal quality. The SE results were confirmed by Raman spectroscopy and SEM analysis.

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Chapter 5

Optical properties of $\text{Cu}_2\text{ZnSnSe}_4$ thin films and identification of secondary phases by spectroscopic ellipsometry

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My contribution to the article

- Idea and the conception of the experiments
- Spectroscopic ellipsometry measurement including optical modeling, fitting and interpretation of the results
- R&T measurement including the data analysis and the interpretation of the results
- Raman spectroscopy measurement including the analysis of the data and the interpretation of the results.
- Most PL measurements including the analysis of the data and the interpretation of the results done by me, PL setup was prepared for the measurement and assistance was given during some measurements by José Fabio López Salas
- Preparation of the HCl etching solution, Br_2 -MeOH solution with the help of Mathias Macke
- Preparation of the samples for the measurements including lift-off process and etching process
- Manuscript design and figure preparation
- Manuscript writing with the input from the co-authors
- Discussion with the referees

Optical properties of $\text{Cu}_2\text{ZnSnSe}_4$ thin films and identification of secondary phases by spectroscopic ellipsometry

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Abstract: We apply spectroscopic ellipsometry (SE) to identify secondary phases in $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) absorbers and to investigate the optical properties of CZTSe. A detailed optical model is used to extract the optical parameters, such as refractive index and extinction coefficient in order to extrapolate the band gap values of CZTSe samples, and to obtain information about the presence of secondary phases at the front and back sides of the samples. We show that SE can be used as a non-destructive method for detection of the secondary phases ZnSe and MoSe_2 and to extrapolate the band gap values of CZTSe phase.

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OCIS codes: (310.0310) Thin films; (310.6860) Thin films, optical properties.

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1. Introduction

In recent years, the quaternary semiconductors $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ (CZTSSe) have been investigated as an alternative absorber to the current thin-film solar cell technologies. Their lower toxicity and higher earth-abundance promise low-cost production and a clean solar cell technology. With a direct band gap in the range of 1.0 eV for CZTSe and 1.5 eV for CZTS with high absorption coefficients of $>10^4 \text{ cm}^{-1}$ slightly above the band gap, this material family has been demonstrated to be suitable for technological application in thin film solar cell devices [1–7]. In laboratory cells, the best-reported efficiency for pure selenide based CZTSe solar cells is 11.6% [8], and for CZTSSe material, it amounts to 12.7%, a promising performance for solar cells [9]. Despite these suitable optical properties and rising interest, there are difficulties in applying this material commercially as an absorber in solar cells. One of the major obstacles is the formation of secondary phases during the growth process, which can be detrimental to the solar cell performance [6, 10–12]. Therefore, it is important to investigate CZTSSe absorbers with a quick and non-destructive method to identify structural properties and the existence of secondary phases. Hence, spectroscopic ellipsometry (SE) is favorable to make fast and non-destructive investigations. SE can be used to collect information on sample structure, the presence of secondary phases and optical properties such as complex dielectric constants, etc [13–15].

In this paper, we focus on the detection of present secondary phases at the front and back interface regions of the CZTSe thin film and the extraction of band gap values of the absorber. We demonstrate an extended optical model which includes multiple interfaces and intermixing layers, to provide a detailed analysis of the sample structure and to identify present ZnSe and MoSe_2 phases, which remain the most prevalent secondary phases in CZTSe absorbers even after process optimization. We obtained all analyzed specimen from solar cell relevant sample batches. Therefore, the presented method and all obtained results are relevant to fundamental investigations as well as for application in solar cell processing and process controlling.

2. Experimental details

2.1 Sample information

In this work, three $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) thin film samples (referred to as Sample A, Sample B, and Sample C) have been investigated by using spectroscopic ellipsometry (SE), spectrophotometry (RT), Raman scattering spectroscopy and photoluminescence (PL).

Sample A and Sample B were fabricated by a high-temperature co-evaporation process, sample C was grown by a two-stage process, i.e. low-temperature co-evaporation with subsequent annealing in Se-SnSe atmosphere. All samples were fabricated at the University of Luxembourg [16,17]. The samples were deposited onto molybdenum (Mo) coated soda lime glass (SLG). The composition of sample A is $\text{Cu}/(\text{Zn} + \text{Sn}) \approx 0.9$ and $\text{Zn}/\text{Sn} \approx 0.94$, and the composition of sample B is $\text{Cu}/(\text{Zn} + \text{Sn}) \approx 0.9$ and $\text{Zn}/\text{Sn} \approx 0.9$. Solar cell efficiencies of companion samples give $\approx 6\%$. The composition of sample C is $\text{Cu}/(\text{Zn} + \text{Sn}) \approx 0.8$ and $\text{Zn}/\text{Sn} \approx 1.2$, efficiencies from similar samples yield $\approx 5\%$. Sample compositions for all samples were measured by Energy Dispersive X-Ray spectroscopy (EDX). Solar cell efficiencies were measured at AM1.5-equivalent excitation.

All SE measurements were done on SLG/Mo/CZTSe samples, as one of the major scopes of this study is the detection of secondary phases at the CZTSe/Mo interface by a non-destructive technique. To confirm the SE results by further methods, i.e. Raman, PL, SEM, etc., the interface region between SLG/Mo and CZTSe was accessed by mechanical lift-off of the absorber with superglue for all samples. Thus, further measurements could be performed on the front and back sides of the absorbers and the remaining substrate surfaces to cross-check SE results.

Sample surfaces were etched before SE measurements to remove oxides and to reduce surface roughness for improvement of the signal-noise-ratios [18]. However, due to the differences in sample morphology and composition, it was necessary to use different etching times and etchants for each sample. Sample A and Sample B were etched with 37wt% hydrochloric acid (HCl) and, sample C was etched by 0.02 M Br₂-MeOH. For each sample, 30 sec etching time was applied before SE measurements. Further, sample A and sample B were etched by HCl before PL measurements for additional 30 sec to improve the signal quality.

2.2 Sample characterization

Spectroscopic ellipsometry (SE) was performed by using a rotating analyzer setup (J. A. Woollam Co, VASE) in the wavelength range from 240 nm to 1700 nm with a step size of 10nm at variable incidence angles (65°, 70° and 75°), on SLG/Mo/CZTSe. Optical reflection & transmission (RT) measurements were performed on lifted-off absorbers on a microscopic glass slide in the wavelength range from 800 nm to 1800 nm by using an integrating sphere. Raman scattering spectroscopy was done with 532 nm (“green” excitation) and 457.9 nm (“blue” excitation) at 3 and 1 mW excitation laser power with a spot size of ~1μm, respectively, in a LabRAM Aramis from Horiba. Photoluminescence (PL) was applied at five different excitation wavelengths (532 nm, 575 nm, 600 nm, 630 nm, and 675 nm) to differentiate between optical transitions of the absorber and present secondary phases. Laser power was kept constant at 2.4 mW with a spot size ~1.5 mm and a detection unit with an InGaAs photomultiplier and a monochromator was used. PL and Raman were measured on the front and back side of each absorber. All measurements were done at room temperature.

3. Results and Discussion

3.1 SE data analysis and optical model design

Spectroscopic ellipsometry (SE) is a non-destructive technique to analyze the optical properties of thin films. However, it is an indirect characterization method because direct conversion of measured parameters (Δ and Ψ) into optical parameters is only valid for very simple cases such as infinitely thick, homogenous and isotropic samples [13]. Therefore, the optical parameters can only be extracted from the measured data by a fitting procedure with an optical model which contains the characteristics of the sample structure, i.e. all present layers in the sample stack with thicknesses and optical functions of each material (ideally from a reference database). Unknown optical functions can be generated based on Fresnel’s equation by using Herzinger-Johs Psemi oscillators [15]. Each Psemi-*M0* oscillator has seven different fit parameters: A- amplitude, E- Center Energy, B- Broadening, WR- Endpoint positions relative to center energy (E), PR- Horizontal position of the right control point relative to the center energy and endpoints, AR- Relative magnitude of the right control points, and O2R- Coefficients for the second order terms in polynomials on the right side of Psemi-*M0* oscillators, respectively. For the fitting procedure, five Psemi-*M0* oscillators were used for each sample. The fitting procedure then contains i) generation of optical functions, ii) translation of these functions via the modeling of the layer structure into theoretical Ψ and Δ , iii) comparison of these calculated values with the measured ones, and then turning back to step i) introducing changes to the oscillators until the best fit for calculated and measured Ψ - and Δ -values is found.

In our previous work, we showed that the detection of a MoSe₂ secondary phase layer at the back interface and the determination of its thickness are possible by data evaluation with a detailed optical model [14]. To generate a more comprehensive model of the investigated samples, we tried numerous different modeling approaches (not discussed in detail here) to introduce a reliable fitting procedure for the characterization of uniformity, crystallinity and interfacial regions and detection of further secondary phases in the sample.

The model design in this manuscript contains CZTSe, MoSe₂, ZnSe, and the Mo substrate layers. We consider MoSe₂ secondary phase in the model because it is easily formed at the CZTSe/Mo interface in many preparation processes due to Selenium (Se) loss to the substrate and decomposition of CZTSe at the backside and the excess Se during the preparation process. In Zn-rich conditions, ZnSe can occur in the whole layer. However, it is often found to segregate at the front or back surface, where its occurrence can be driven by decomposition reactions of the CZTSe absorber [19]. As discussed in Section 2.1, only sample C shows Zn-rich composition at the end of the process. However, SIMS profiles of the complete solar cells for sample A and sample B show Zn and Se accumulation at the back side of absorbers (not shown here). Therefore, for all three samples, ZnSe secondary phases are taken into consideration. The optical functions for ZnSe and Mo were inserted into the model from the database of the WVASE software; MoSe₂ was taken from our previous investigation [14]. The optical function of CZTSe was then extracted by the described fitting procedure. Our applied model includes (top to bottom) an EMA surface roughness layer (Bruggeman effective medium approximation [13]) with a 50:50 void:top layer mixture, an EMA ZnSe:CZTSe layer with a variable fraction, the actual CZTSe absorber, a standard intermix layer for modeling the non-ideal interface (EMA with 50:50 mixture of neighboring phases), a ZnSe layer, another standard intermix layer, a MoSe₂ layer, another standard intermix layer, and the Mo substrate. The intermix layers were set to a constant value and are not included as fitting parameters. We found that a thickness of only 1nm is already sufficient to account for the non-ideal interface between neighboring layers. Further reduction or the total absence of these layers lead to significantly worse fitting results. Furthermore, we find that these layers strongly reduce the correlation between neighboring layers and are essential for achieving unique fitting results. The structure of the optical model is illustrated in Fig. 1.

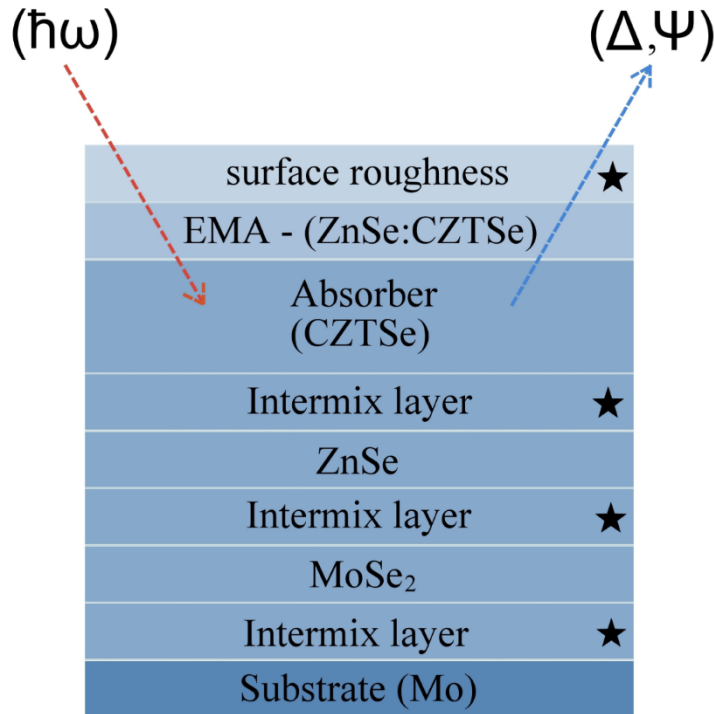


Fig. 1. Schematic representation of the multi-layer optical model for SE data analysis. Layers labeled with a star are based on Bruggeman Effective Medium Approximation (EMA), with a 50:50 mixture of adjacent layers. The ZnSe: CZTSe EMA layer contains a variable fraction which is varied in the fitting procedure.

Figure 2 shows experimental Ψ and Δ data for each sample together with the fitted curves from the modelling. For better viewing only the results for the 70° angle is shown. SE data for the energy range between 410 nm-1700 nm (3.0 eV and 0.75 eV) was used for all samples in the fitting procedure. Data points below 410 nm (above 3.0 eV) were not considered for the fit, due to high signal noise. This occurrence of noise was observed for many polycrystalline CZTSe thin film samples. The origin of the noise could not be identified with certainty, but it might originate from inhomogeneities, surface roughness and/or other artefacts at the front side of the sample such as intermixing of small amounts of further secondary phases.

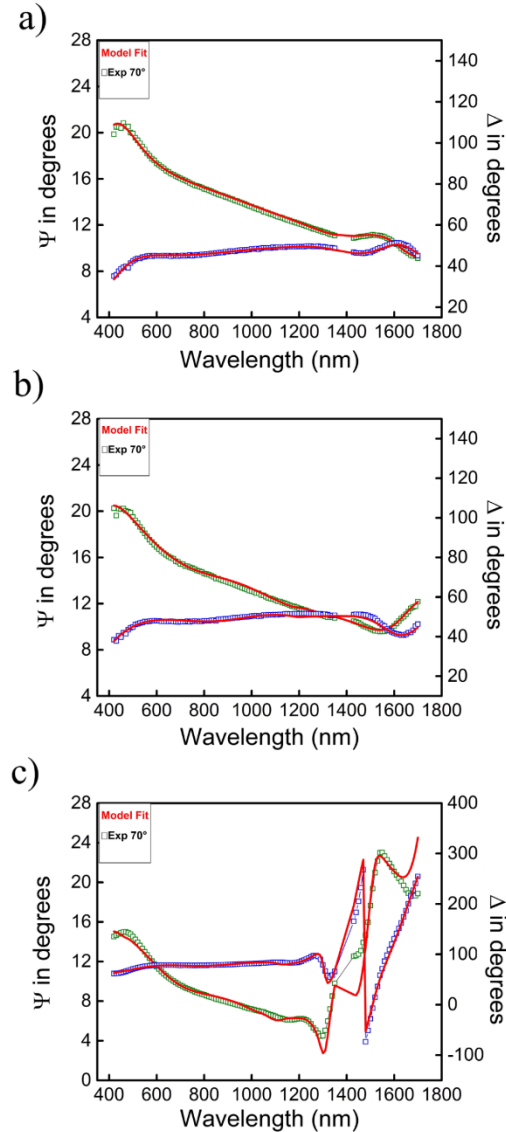


Fig. 2. Measured and fitted ellipsometry data for samples A, B, and C, respectively. Psi (Ψ , green colored symbol) and Delta (Δ , blue colored symbol) values are shown for only one incidence angle (70°) together with the fit results (red solid lines)

The thicknesses of layers extracted from the fitting procedure along with their standard deviations are presented in Table 1 for each sample. All samples show a thickness of the surface roughness layer which is in the usual range for SE evaluations. However, the value for sample B appears very low. Note, the fitted numbers for the surface roughness usually do not reflect the real surface roughness values of the sample. They may rather give an indirect indication for the actual roughness of the surface. The fitted numbers are influenced further by the morphology/shape of the grains, lateral inhomogeneities of the optical function and of the roughness itself. Nevertheless, the extracted thicknesses for the absorbers and the MoSe_2 layer for sample C are supported by SEM results, as shown in Table 1.

According to fitting results, each sample has ZnSe and MoSe_2 secondary phases on the back side of the absorber, with different amounts, showing by far the highest MoSe_2 amount for sample C. Further, only Sample C shows ZnSe fractions on the front side of the absorber. The different amounts of MoSe_2 and the ZnSe:CZTSe mixture on the front side of sample C can be explained by the different processing routine for sample C compared to samples A and B, and will be discussed further below. The mean square error (MSE) which shows the fit quality indicates a very good fit for samples A and B, whereas the MSE for sample C is significantly larger. This can be explained by a higher degree of inhomogeneities and worse crystal quality of the absorber due to the distribution of ZnSe secondary phases, or higher disorder in the crystal for the case of sample C, compared to sample A and B. In fact, scanning electron microscope (SEM) pictures from samples A and B show ZnSe inclusions at the backside of the CZTSe film (not shown here). In contrast to this, sample C does not show any ZnSe inclusions but may rather contain a network of ZnSe nanodomains which percolate the entire CZTSe film. An earlier investigation on samples prepared by the same procedure as sample C revealed this network of ZnSe nanodomains by atom probe tomography [20]. A network of two phases as described is hard to model by this approach. The modeling of such a network would be possible with a strongly modified model which includes a Maxwell-Garnett EMA instead of the widely used Bruggeman EMA [21,22]. We do not follow this approach due to its higher complexity and because it does not reflect a general optical model for the whole set of samples. This deficit of the presented optical model for sample C can additionally lead to a worse MSE in the fitting procedure for the SE data as described above. Nevertheless, we can still state that this model is at least sufficient to determine the presence of ZnSe secondary phases for each sample.

Thickness values extracted from SEM measurements (see Table 1) confirm the thicknesses from SE for the absorber and for the MoSe_2 layer (sample C). Further, the presence of ZnSe secondary phases is confirmed by SEM (sample A and B) and by APT (sample C), as described above, respectively.

Table 1. Fitting results of the optical model including the thicknesses and their standard deviations are shown for surface roughness, EMA layer with the ratio of components, CZTSe absorber layer, the interface layer. Mean Square Error (MSE) from SE, and the thicknesses of absorbers MoSe₂ layers from SEM.

Energy fit range 0.75-3.0 (eV)	Roughness (nm)	EMA layers (nm)	CZTSe (nm)	Interface layer (nm)		MSE	SEM results (nm)	
		(ZnSe: CZTSe)		ZnSe	MoSe ₂		CZTSe	MoSe ₂
Sample A	14.0±0.1	8.11±6.8 (0.0:100) ±6.3	1086±8.7	4.0±3.5	4.0±3.9	1.7	1150 ±150	≈0.0
Sample B	2.3±0.2	9.5±5.0 (0.5:99.5) ±2.1	1033±18	26±15	26±13	3.1	950 ±150	≈0.0
Sample C	12.0±0.5	9.2±1.6 (40:60) ±6.6	1242±43	18±13	236±4.6	26.4	1200 ±100	185±5 0

3.1.1 Band gap calculation

To calculate the band gap of CZTSe thin films, the refractive index and extinction coefficient were extracted from the SE results. The optical absorption coefficient “ α ” of CZTSe can be calculated by the expression of $\alpha = \frac{4\pi k}{\lambda}$ where k is the extinction coefficient, and λ is wavelength. Additional to this, we calculate the absorption coefficient by optical reflection and transmission measurements by using the formula $\alpha = -\frac{1}{t} \ln \frac{T}{(1-R)^2}$ where “ t ” is the film thickness (determined by SE fitting results and SEM), R and T are reflectance and transmittance, respectively.

The relationship between absorption coefficient and photon energy for a direct semiconductor is [23]:

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (1)$$

Where A is constant, $h\nu$ is the photon energy, E_g is the band gap. Optical band gap can be calculated by extrapolating the linear region of $(\alpha h\nu)^2$ versus $h\nu$. In Fig. 3 a) and b), we show the extraction of the band gap by this approach for SE and R&T results, respectively. The found band gap values from SE measurements amount to 0.99 ± 0.02 eV for sample A and 0.97 ± 0.01 eV for sample B. Surprisingly the behavior of sample C shows two possible transitions at 0.93 ± 0.01 and 1.020 ± 0.001 eV. We explain this behavior by the discussed fact that sample C does not contain a single phase kesterite bulk, but rather a network of CZTSe and a ZnSe secondary phase. Due to a superposition of the signal response of these two phases which, as discussed above, cannot be resolved by our model, the extracted absorption coefficient may include artefacts. Due to this restriction of our approach we are not able to distinguish such an artefact caused by the discussed network structure from a further transition in CZTSe, e.g. caused by second band gap or regions with different band gap [5,20]. Nevertheless the photon energies of the observed transitions are in the range of reported band gap values [24–27]. Note, the extracted absorption values for sample C are

lower than for the other two samples. Therefore, a multiplication factor of 4 is operated for sample C.

The evaluation of the R&T measurements gives band gap results of 0.99 ± 0.02 eV, 0.94 ± 0.01 eV and 0.99 ± 0.01 eV for sample A, sample B, and sample C, respectively. The differences in band gap values between samples can be explained by different order-disorder ratios and different compositions [28]. Furthermore, the existence of secondary phases may lead to distortions of the extracted absorption spectra due to superpositioning of optical transitions of different phases [29]. However, band gap results are similar for both techniques. The slight discrepancy in the results for both methods can be explained by their different sensitivities for bulk and surface. R&T is a bulk sensitive method, giving equal weight to all parts of the entire layer. For SE we can expect a higher influence of the surface region (depending on layer thickness, probing wavelength and absorption coefficient). Due to the ambiguity of the fitting regions for the linear extrapolation the extracted values contain a systematic error. The given error was determined from extrapolations for varied fitting regions for each spectrum.

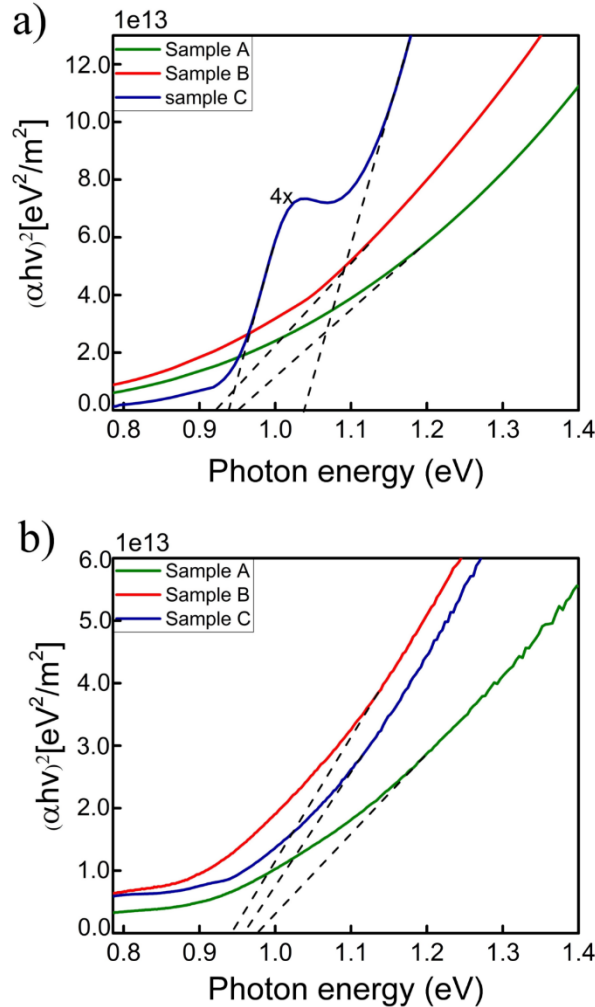


Fig. 3. The plot of $(\alpha hv)^2$ vs. $h\nu$ from a) SE results b) R&T results for all samples and extraction of band gaps via linear extrapolation to zero (dashed lines).

3.2 Raman results

Raman spectroscopy was performed on the front and back side of absorbers and the SLG/Mo substrate after lift-off process for each sample at 532 nm and 457.9 nm excitation wavelengths. The reason for using a second excitation wavelength is to identify small amounts of ZnSe in the absorber. To represent a large area of the samples, the average of four different areas is shown in Fig. 4. The Raman signal from ZnSe secondary phases in CZTSe is strongly enhanced due to the resonant Raman effect for the 457.9nm laser, as the energy of its photons is in the region of the band gap energy of ZnSe (~ 2.7 eV). Hence, even very small ZnSe fractions in the sample can be identified with the “blue” excitation laser [10,30]. The utilization of solely the 532 nm excitation can only reveal very large amounts of ZnSe in the sample. Therefore, “green” excitation is not sufficient to reliably detect ZnSe secondary phases in CZTSe samples.

The Raman results for the 532nm excitation show the expected CZTSe fingerprints for the front side of the absorbers (Fig. 4a) without any indications for secondary phases. However, at 457.9 nm laser excitation, sample C shows additionally a ZnSe peak at 250 cm^{-1} , whereas a clear CZTSe fingerprint without indication for any secondary phases is confirmed for samples A and B. These results are in agreement with the SE results as discussed before in Section 3.1, i.e.: no indication for ZnSe at the front side of sample A and sample B neither by SE nor by SEM. and co-existence of ZnSe with CZTSe at the front side of sample C. Furthermore, as discussed above a reported APT study on similar samples shows the existence of a ZnSe network in the entire absorber [20].

At 532 nm excitation wavelength, the Raman measurements on the back side of the absorbers (Fig. 4b) show clear CZTSe fingerprints without any indication of secondary phases. However, at 457.9 nm excitation wavelength, all three samples show a clear ZnSe peak at 250 cm^{-1} which is in accordance with SE results (see Table 1).

The Raman modes for CZTSe are still visible in all samples for 457.9 nm, however with very low intensities for samples A and B, at which the second main peak around 175 cm^{-1} is hardly visible. In contrast, both main CZTSe peaks are still fairly distinguishable for sample C. This different behavior of samples can be explained by the different growing process which leads to a different distribution of ZnSe secondary phases as discussed in Section 3.1. ZnSe secondary phase in sample C is distributed as a network in entire bulk. Therefore, a clear appearance of peaks for both phases CZTSe and ZnSe is expected. In contrast, sample A and sample B contain ZnSe inclusions at the back side of the absorber, which may hamper the detection of CZTSe for sample A and sample B, resulting in the very low intensity of CZTSe peaks.

Raman spectra for the remaining substrate (Fig. 4c) show MoSe_2 peaks for all three samples. However, the MoSe_2 peak intensities of sample A and sample B are much lower than the MoSe_2 intensity of sample C. Therefore; these two spectra were multiplied by a factor of 5 for better viewing. Raman spectroscopy results are in good agreement with SE results, which show by far the highest thickness (amount) of the MoSe_2 secondary phase for sample C (see Table 1).

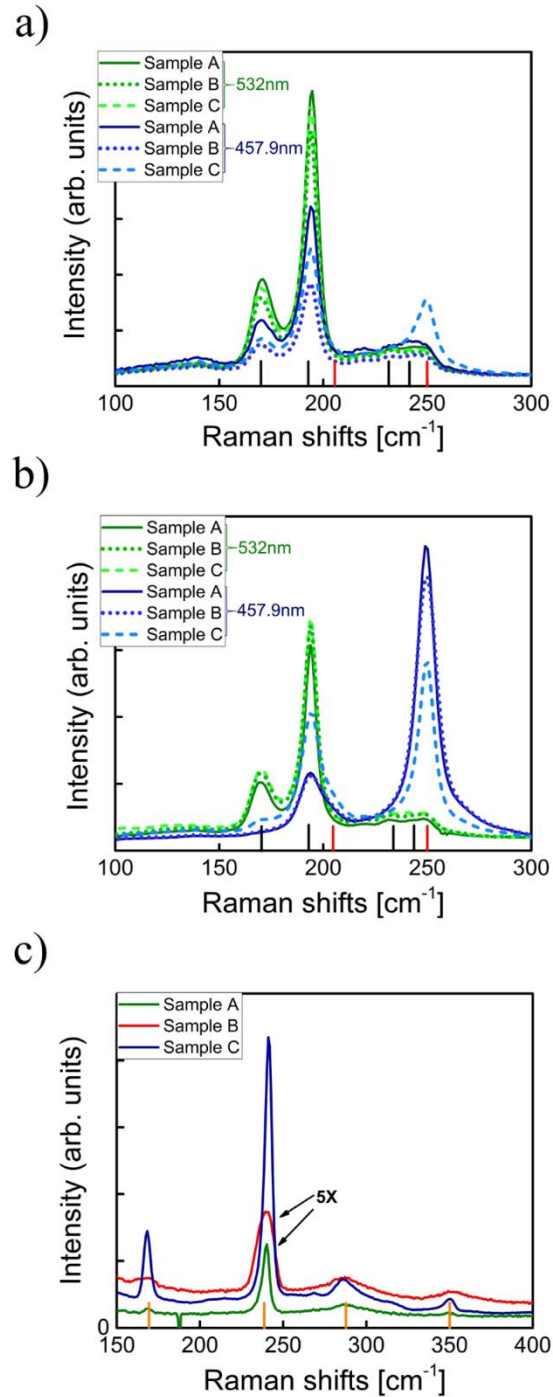


Fig. 4. Raman spectra for each sample (a) front side of the samples, (b) back side of samples and (c) the remaining substrate after lift-off process. Excitation wavelengths are indicated in a) and b) by green and blue lines for 532nm and 457.9 nm, respectively. In figures a) and b) the black and red markers show the peak positions of CZTSe and ZnSe phases. In figure c) orange markers show MoSe₂ peaks.

3.3 Photoluminescence results

PL spectroscopy was performed on the front and back side of the absorbers with different excitation wavelengths. The aim of using different excitation wavelengths was to distinguish between optical transitions of the absorber and present secondary phases. PL spectra can also be used to determine the band gap of a semiconductor if the material has no tailing and the emission is dominated by band to band transition. However, it is not the case for CZTSe and the main PL peak is usually observed around 100 to 150 meV below the band gap energy due to tailing and the contribution of defects [31,32].

In Fig. 5, we show the PL spectra for each sample. Note, that the plotted spectra show the averaged result from two different areas to represent a large area of the sample. The maximum PL position of the main peak from the kesterite occurs for all samples in the range 0.83-0.86 eV, with no correlation to the discussed band gaps of the samples. The slight differences between the PL peak positions can occur due to different compositions, which may lead to different tailing properties and other dominating defects. The PL spectra from the backside of each absorber show additionally a broad peak at around 1.2 eV, known as a ZnSe defect transition in literature [30,33–35]. These results are in good agreement with SE and Raman results: All samples show clear evidence for the existence of ZnSe secondary phases at the back side of the absorber for both SE and Raman spectroscopy (see Table 1 and Section 3.2).

The intensity of the ZnSe defect transition peak depends on the applied excitation wavelength: with increasing excitation wavelength, the intensity of this defect transition diminishes. This demonstrates that the defect transition can be probed selectively by the choice of the wavelength. Sufficiently short wavelengths (higher photon energies) are necessary to excite the involved defect states. Further, by choosing long wavelengths, the ZnSe defect transition can be excluded from the spectrum to allow for measuring only the PL from CZTSe. This clean-up procedure is necessary for more complex evaluations of the high energy wing of the CZTSe PL for e.g. extraction of quasi-Fermi level splitting by Planck's generalized law [36–38].

For the front side of the absorbers, only the measurement with the shortest excitation wavelength (532 nm) is shown in Fig. 5, since no differences between the results from different excitation wavelengths could be observed (not shown here). The PL maxima for the front side match the peak positions found on the back surfaces. Further, none of the PL spectra shows any contribution from ZnSe. This is in accordance with SE and Raman results for samples A and B. However, both SE and Raman results show clear indications for ZnSe at the front side of sample C. This discrepancy can be interpreted as an indication of a higher sensitivity of SE and Raman spectroscopy for the detection of small fractions of ZnSe secondary phase in CZTSe samples.

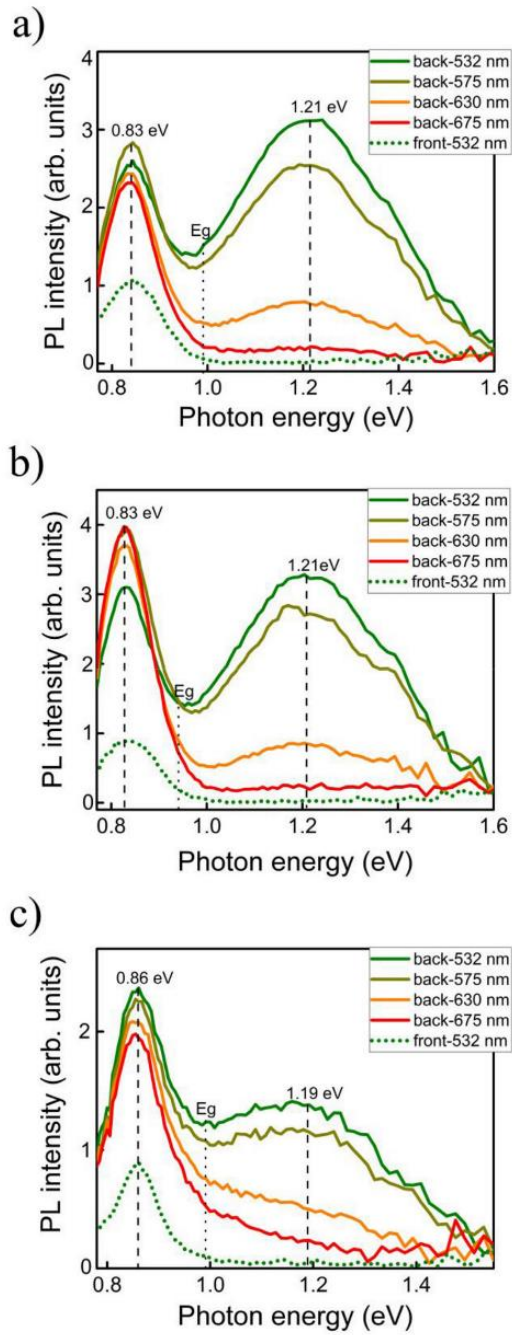


Fig. 5. PL spectra for a) sample A, b) sample B, c) sample C, respectively. Solid lines represent the backside of each absorber for different excitation wavelengths, these are given in the legend and are color coded, respectively. Dotted lines represent the front side of the absorbers for only 532 nm excitation. The band gap from R&T measurements is indicated in the plot.

4. Conclusions

In this paper, we have demonstrated that SE can be used as a non-destructive technique to detect secondary phases within a layer and/or at the back side of the absorber (SLG/Mo/CZTSe). The existence of MoSe₂ at the back side and its amount can be determined by SE. Additional to this, the presence of ZnSe at the front and back side of the absorber can be determined by SE. The results are confirmed by Raman and PL spectroscopy.

We use a complex optical model based on a multi-layer approach for evaluation of SE data. The construction of an optical model which also contains all minor constituents in the sample, such as fractions of secondary phases, is critical to making accurate interpretations on the properties of the material. If this requirement is met, SE allows for accurate extraction of optical parameters such as band gap, refractive index, and extinction coefficient. The results show that band gap determination by SE is as reliable as R&T measurement, and works on CZTSe on Mo substrates in advantage over R&T. The slight discrepancy of results extracted from both techniques is due to the different sensitivities for bulk and surface.

We also observe that the intensity of the ZnSe defect transition peak in PL shows a dependency on the applied excitation wavelength. Therefore, it is important to select the wavelength adequately for selective excitation or removal of the ZnSe defect transition in the measured PL spectra.

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Chapter 6

Influence of Cu-Zn disorder in $\text{Cu}_2\text{ZnSnSe}_4$ absorbers on optical transitions: A spectroscopic ellipsometry study

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My contribution to the article

- Idea and the conception of the experiments
- Spectroscopic ellipsometry measurement including optical modeling, fitting and interpretation of the results
- Raman spectroscopy measurement including the analysis of the data and the interpretation of the results.
- Most PL measurements including the analysis of the data and the interpretation of the results done by me, PL setup was prepared for the measurement and assistance was given during some measurements by José Fabio López Salas
- Preparation of the etching solution $\text{Br}_2\text{-MeOH}$ with the help of Mohamed H. Sayed
- Manuscript design and figure preparation
- Manuscript writing with the input from the co-authors
- Planned: updating the manuscript with the reviewer's comments.

Influence of Cu-Zn disorder in $\text{Cu}_2\text{ZnSnSe}_4$ absorbers on optical transitions: A spectroscopic ellipsometry study

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Abstract: Spectroscopic ellipsometry is applied to investigate the effect of Cu/Zn disorder in a $\text{Cu}_2\text{ZnSnSe}_4$ crystal on the optical transitions. We observe that the degree of order has an impact not only on the first optical transition E_0 at the gamma point, which is the commonly discussed direct band gap in kesterites. It also varies the further optical transitions E_1 and E_2 which involve the upper band gaps. While E_0 shows an increasing trend with higher degree of order, the transitions E_1 and E_2 show an opposite behavior, indicating a fundamental impact of disorder on the shape of the band curvature in $E(k)$ space.

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1. Introduction

The interest of quaternary semiconductors $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ abbreviated (CZTSSe) has been rapidly increased in the last decades due to the demand on abundant eco-friendly materials and low-cost production process. Especially, CZTSSe absorbers are promising candidates for the next generation thin film solar cell devices due to their optoelectronic properties, i.e., the direct band gap of CZTSSe (varying from 1.5 eV S-based kesterite (CZTS) to 1.0 eV Se-based kesterite (CZTSe)) and high absorption coefficient of the materials ($>10^4 \text{ cm}^{-1}$) [1-5]. However, the reported highest efficiency of CZTSSe in the laboratory cells (12.7%) [6] is far from that of established thin film solar cell technologies such as $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ and CdTe [7]. The reasons for the performance gap are the formation of deep defect levels, defect complexes, and the existence of unwanted secondary phases during the growth process [8-9].

Experimental and theoretical studies have reported that CZTS and CZTSe both have kesterite crystal structure with varying degrees of order of the Cu and Zn atoms within the Cu-Zn planes at $z=1/4$ and $z=3/4$. This disorder leads to the formation of Cu_{Zn} and Zn_{Cu} antisite defects [4,8,10-12]. They have different impacts on the solar cell efficiency, e.g., the Cu_{Zn} antisite defect is deeper than the Copper vacancy (V_{Cu}), but it contributes to the p-type nature of the CZTSe material. However, Zn_{Cu} antisite defect is not favorable and causes a shallow level near the conduction band [8]. Therefore, it is important to understand the transformation mechanism of Cu-Zn atoms in CZTSe samples to improve the solar cell efficiency.

Rey et al. [10] reported that there is a critical temperature T_c for CZTSe absorbers above which the Cu-Zn atoms are fully disordered. The value of which is about $\approx 200 \pm 20$ °C. Temperature treatments below T_c

shown to enhance the degree of order on the Cu/Zn sites and the perfectly ordered state can be reached only at 0 °K [10,13].

When disorder of Cu-Zn atoms occurs in the crystal, the fundamental band gap (E_0) of the CZTSe absorber increases with increasing ordering due to the change in bond length along the volume deformation and also the change in electron-phonon interactions [4,10]. Below the critical temperature, CZTSe tends to show a more ordered structure, and the fundamental band gap increases with the ordering of the Cu-Zn sites, and it is vice versa in the case of disordering above the critical temperature [10]. This optical transition E_0 occurs from the valence band maximum VBM to the conduction band minimum CBM at the gamma point [4].

Recently published papers only report the impact of the degree of order on the fundamental band gap E_0 of CZTSe absorbers and its effect on solar cells [10,14-16]. However, only a few theoretical and experimental reports show that the electronic band structure of CZTSe has a second gap in the Energy dispersion $E(k)$ diagram due to the Sn contribution of CZTSe, which does not overlap with the conduction bands at higher energy [4,17]. Therefore, this lone CB leads to a separation between topmost CBs which leads to a second band gap in the CZTSe. Although several studies have shown the impact of order/disorder on the first fundamental band gap [10,14-16], the effect on the further transitions has not been studied yet, which is calling for further investigations. In this study, we aim to shed light on this issue, i.e., the impact of the degree of order/disorder on the higher optical transitions of the CZTSe material. For this purpose, we use Spectroscopic Ellipsometry (SE), as this is a favorable tool to investigate any optical transitions in semiconductors. By examining the complex dielectric function, information on optical transitions can be obtained which are closely related to the electronic band structure of the semiconductor material. The features of complex dielectric functions are related to interband structures of the material, i.e., critical points (CPs) [18].

2. Experimental details

In this work, the studied CZTSe sample was fabricated on a bare soda lime glass substrate by a high-temperature co-evaporation process at the University of Luxembourg. The composition was measured by Energy Dispersive X-Ray Spectroscopy (EDX) and is Cu-poor ($\text{Cu}/(\text{Zn} + \text{Sn}) \approx 0.80$) and Zn-rich ($\text{Zn}/\text{Sn} \approx 1.2$). Companion samples which were grown on glass/Mo substrates show a solar cell efficiency in the range of 5-7 %. The values were measured at AM1.5-equivalent excitation. The structural properties of the sample and the growth process are described in detail elsewhere [19].

Prior to SE measurement, the CZTSe sample was etched for 30 sec by 0.02M Br_2 -MeOH to reduce the surface roughness and to improve the signal- noise ratio [20,21]. The reduction of the surface roughness was also confirmed by Atomic Force Microscopy (AFM), which gives the values of ~ 114 nm and ~ 65 nm before and after etching, respectively. The corresponding numbers from SE extracted from the EMA surface layer evaluation (discussed later) are ~ 45 nm and ~ 10 nm, respectively. Note that, the surface roughness from AFM usually does not match the roughness received from SE, as the latter one is obtained by an effective medium approximation which is affected by the optical model and the length scales of the

surface inhomogeneities of the sample. However, both techniques confirm a significant reduction of the surface roughness. Additionally, the back side of the substrate (glass) was roughened to suppress the backside reflection during SE measurements.

Different steps of heat treatment were applied whereas the parameters temperature and time were controlled, in order to provide different degrees of Cu-Zn order in the crystal structure. All heat treatments were done in an N₂ atmosphere with the help of a hotplate and rapid quenching. The CZTSe sample was first transformed to the disordered level by heating at 250 °C for 2 h (referred to as sample A). Then, the degree of order was increased step by step by annealing at 125 °C for 2 h for each annealing step, resulting in various states of ordering (referred to as sample B, C, D, E, F, respectively). The degree of ordering increases step by step from A to F. The procedure for the heat treatment is shown in Fig. 1. After each heat treatment step, the sample was characterized by SE, Raman and Photoluminescence (PL).

SE was applied to determine the optical constants, SE was measured in the spectral range from 240 nm to 1700 nm with different incident angles (65°, 70°, and 75°) in a setup containing a rotating analyzer (J. A. Woollam Co, VASE). Raman spectroscopy and PL were performed as well for verification of the targeted degree of order in the crystal. Raman spectroscopy was applied in a LabRAM Aramis from Horiba setup with the 532nm excitation wavelength at 3 mW, and the spot size is ≈1 micrometer. PL spectroscopy was performed with a detection unit containing an InGaAs photomultiplier and a monochromator. The excitation wavelength is 532nm and the spot size ≈1.5 millimeters for PL spectroscopy. All measurements were done at room temperature.

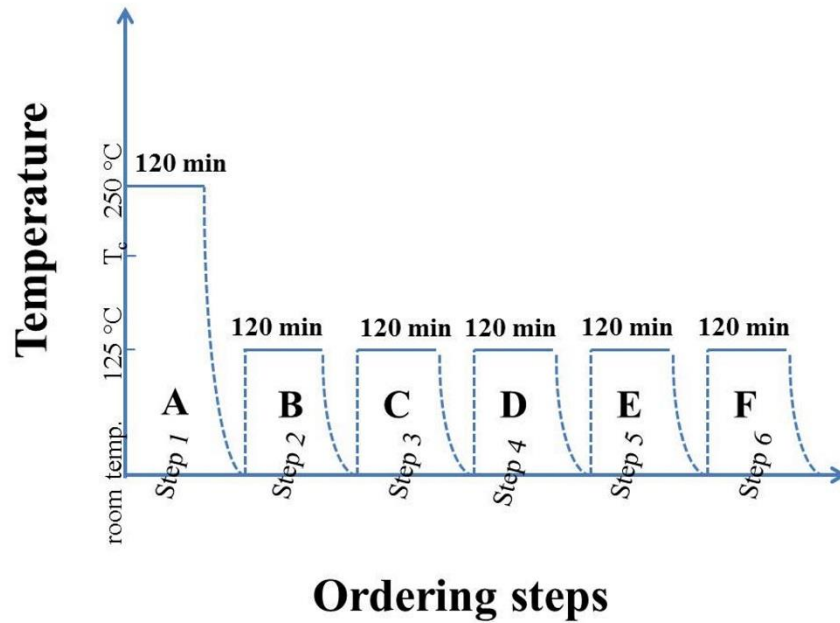


Fig. 1. Schematic representation of the heat treatment procedure.

3. Results and Discussion

3.1 Spectroscopic Ellipsometry Results

Spectroscopic Ellipsometry (SE) is a non-destructive technique to measure a change in polarization when the light is reflected from or transmitted through the sample structure. The measured parameters Psi (Ψ) and Delta (Δ) describe the amplitude ratio and phase difference upon reflection, respectively. As a drawback of SE, these parameters cannot be directly converted to optical properties of the material [22]. Therefore, to determine the optical and structural features of the material, it is necessary to develop an optical model. Therefore, reference samples can be used from a SE database (J. A. Woollam Co, VASE). However, if the analyzed material does not exist in the SE database or the material properties varies in horizontal or longitudinal direction, it is necessary to start from scratch to compose a full optical model. Thus, oscillator functions are used to describe the dielectric functions and to obtain material properties, such as thickness, surface roughness, complex optical constants, etc. After the development of an optical model, a fitting process is required between experimental data and modelled data, in order to optimize the model parameters. This fitting process can repeat until reaching the best match between experimental and modelled data. At the end of the fit cycle, the wanted sample properties such as the complex refractive index or the complex dielectric constants, film thickness, surface roughness, etc. can be obtained.

In this study, we use Herzinger-Johs Psemi oscillators to describe the material properties as discussed above. These oscillators are flexible and designed to fit the dielectric constants of semiconductors or other crystalline materials. More details about this oscillator type can be found in Ref. 23.

Our model consists of a Bruggeman Effective Medium Approximation (EMA) surface roughness layer (50:50 mixture of void and CZTSe), CZTSe-bulk layer, EMA layer (CZTSe: Void), and a glass substrate, respectively. The EMA surface roughness layer was considered to account for the roughness of the sample. Secondly, another EMA layer was considered between the CZTSe absorber and the glass substrate to account for the voids in the backside region of the CZTSe absorber. Fig. 2 represents the structure of the optical model for SE data evaluation.

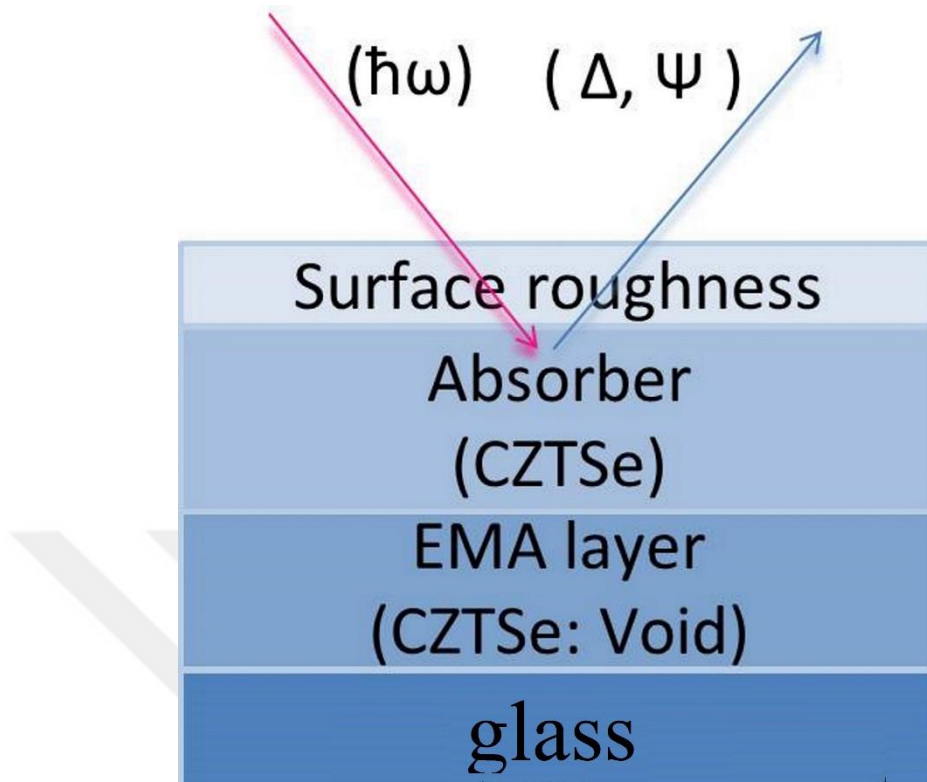


Fig. 2. Schematic representation of the designed optical model for SE data analysis

Although SE was performed in the energy range of 0.72-5.16 eV (1700-240nm), the fitting procedure was limited to the energy range between 0.72 eV and 4.5 eV. The higher energy range was excluded from the fitting procedure due to noisy signal, to avoid artefacts and lower fit quality. The possible origin of the noisy signal in the high energy range might be caused by inhomogeneities, surface roughness or other artifacts at the front side of the sample.

Figure 3 shows SE fitting results (Ψ and Δ in degrees) for only a minimum and maximum degree of order achieved in this study, respectively. The sample with the lowest degree of order is referred to A, and the highest degree F.

Using the same number of oscillators for the fitting procedure for each state of ordering, the shape of the oscillators (such as position, amplitude, broadening parameter, etc.) had to be adapted, to obtain good fit results at the end of the fitting procedure. Surprisingly, we did not observe any trend for the oscillator parameters for different degrees of ordering.

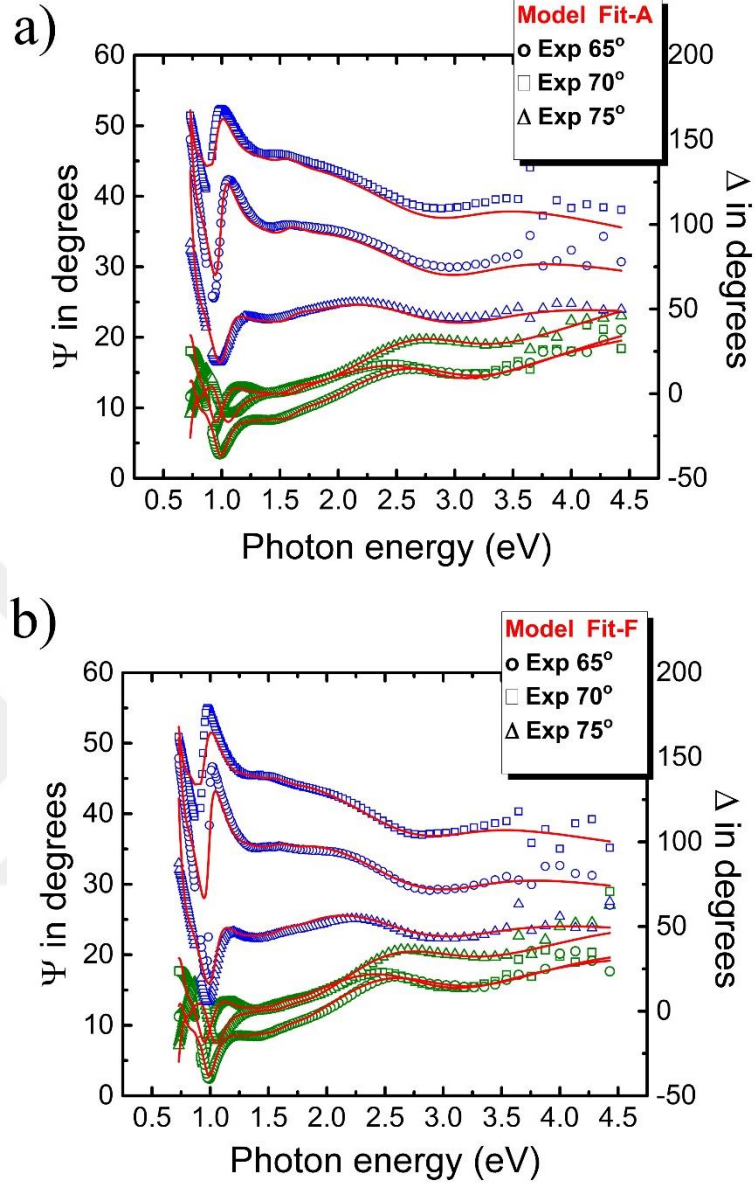


Fig. 3. Ψ and Δ fitting results of the CZTSe sample a) lowest degree of ordering (sample A), and b) highest degree of ordering (sample F) reached in this study, respectively. Green symbols: Ψ , blue symbols: Δ , red solid lines: model fit

After the fitting process for each sample, the imaginary parts of the extracted complex dielectric functions “ ϵ_2 ” were compared with each other to see the effect of the degree of order on the optical transitions, i.e., the threshold energies of the absorption coefficient and critical points (CPs).

As discussed above, the complex dielectric function at different wavelength allows to obtain information about the electronic band structure of the semiconductor material, and the features of the complex dielectric functions are related to interband structures of the material, i.e. CPs [18]. Choi et al. showed the CP at $E_1 \approx 2.42$ eV (from the VBM and CBM at the $Z(0,0,0.5)$ point of the first Brillouin zone) for optical transitions in CZTSe by SE [24]. Fig. 4 shows the comparison of ϵ_2 for each sample. We observe that the peak position of ϵ_2 varies from 2.40 eV to 2.36 eV for different degrees of Cu/Zn ordering.

The photon energy of this feature ~ 2.40 eV corresponds to the transition E_1 and shows a decreasing trend with increasing degree of order.

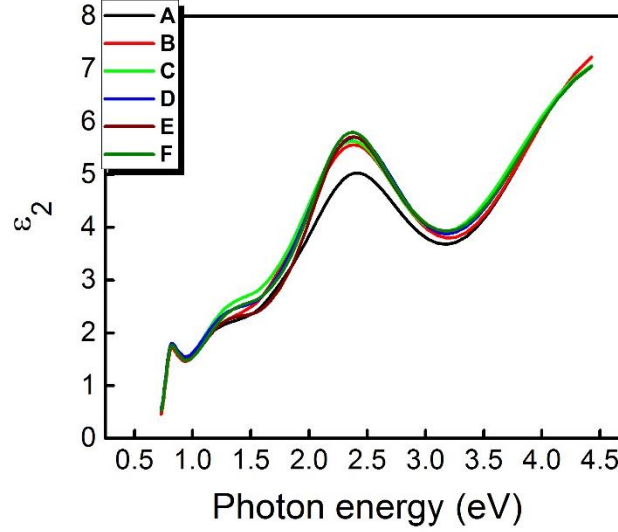


Fig. 4. Comparison of the imaginary part of complex dielectric functions ϵ_2 for all sample states, i.e., the degree of ordering of the sample.

3.1.1 Optical Transitions in CZTSe

The evolution of the fundamental band gap with the degree of ordering is well known in the literature [10,13], i.e., the fundamental band gap value E_0 increases with increasing degree of order. Due to the direct transition from VBM to CBM at Γ (0,0,0) in CZTSe, the fundamental band gap E_0 can be extracted by linear extrapolation of $(ah\nu)^2$ versus $h\nu$ [1-4,24].

To calculate the absorption coefficient α , we can use the relation between α and k , which is expressed by $\alpha = \frac{4\pi k}{\lambda}$, where k is the extinction coefficient, λ the wavelength. The refractive index n and k were extracted from the SE results, as shown in our previous study [25]. Fig. 5 shows the differences in the absolute values of the fundamental band gap E_0 for different degrees of order. The inset displays Tauc's plot $(ah\nu)^2$ versus $h\nu$, as extracted from SE data for state.. The relative energy difference between the most ordered and most disordered state in our study is 60 meV. This result is in good agreement with previously reported values [10,15,16]: starting from a preferentially disordered state and evolving to higher degrees of order, the fundamental band gap E_0 is increasing. However, the absolute band gap values of each sample appear slightly higher when compared to some reported values [4,10,26]. One explanation for the high absolute values is a possible systematic error due to the modelling approach which impacts the fitting regions for the linear extrapolation. On the other hand a few publications report on slightly higher values which are similar to our extracted results [10,27,28]. In literature, there are some discrepancies for reported E_g values of CZTSe due to the uncertainties of E_g extrapolations, say, any method shows another band gap value.

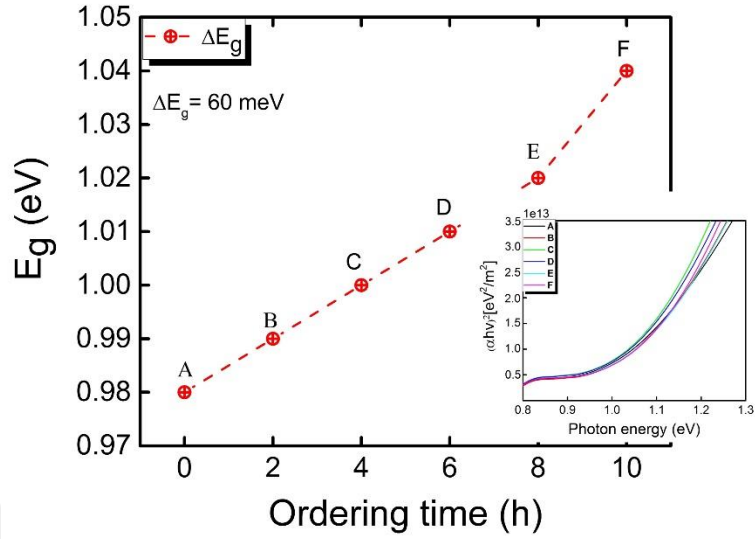


Fig. 5. Fundamental band gap for different degrees of order, inset: Tauc plot $(\alpha hv)^2$ versus $h\nu$ from SE data for each state.

The further transition E_1 is not as well known as the first transition E_0 at Γ (0,0,0) in the literature [4,18,24,29,30]. This transition E_1 might be in the region of the Z(0,0,0.5) point of the first Brillouin zone, and it can be either a direct or indirect transition due to the flat band dispersions [4]. For a better understanding of the transition pattern of E_1 , it is necessary to extrapolate the values of the linear region of $(\alpha hv)^2$ versus $h\nu$ or $(\alpha hv)^{0.5}$ versus $h\nu$, related to the possible transition cases (i.e., direct or indirect transition, respectively). These results are shown in Fig. 6. The inset given the Tauc plots for both E_1 and E_2 transitions for each sample state, respectively.

We observe that the linear region of $(\alpha hv)^2$ versus $h\nu$ or $(\alpha hv)^{0.5}$ versus $h\nu$ at around 2.0-2.5 eV shows a red-shift behavior, i.e., the pattern of E_1 indicates a decreasing trend with increasing ordering degree of the sample. These results are in good agreement with SE results in the behavior of the peak position of ε_2 at around 2.4 eV in Fig. 3. Additionally, it can be noted that this trend is valid for each transition case assumed.

The next visible higher transition E_2 at around 3.5 eV shows a similar behavior like E_1 , i.e., the pattern of further transitions (E_1 and E_2) displays a decreasing trend with increasing degree of order in the CZTSe sample. The observed trend is independent from the transition type (direct or indirect).

The optical transitions found in our study ($E_0 \approx 1$ eV at Γ (0,0,0), $E_1 \approx 2.4$ eV suggested at Z (0,0,0.5) and $E_2 \approx 3.5$ suggested at Z (0,0,0.5) points of the first Brillouin Zone of the CZTSe) show a clear dependence on the Cu/Zn disorder in the CZTSe absorber, i.e., while E_1 and E_2 indicate a red shift with increasing degree of order, E_0 reveals a blue shift for a higher ordered crystal. This opposite behavior of the optical transitions in CZTSe can be explained by a change in the shape and different curvature of the band in the $E(k)$ space. Consequently, the latter effect might impact the transport properties of the semiconductor material due to the relationship between the conduction band or valence band curvature and the effective mass m^* of electrons, which determines the mobility μ , which decreases with increasing

m^* [31]. We speculate that the degree of ordering in the CZTSe crystal has an impact on m^* and, therefore, on μ , resulting in changing transport properties. Our anticipation would give a new point of view on the results discussed by Rey et al. [14]. In this report, a slight improvement in solar cell efficiency was shown for the CZTSe samples with the highest degree of order. They noted that the solar cell device which has higher efficiency shows a lower current and a higher open circuit voltage V_{oc} both effects explained by the higher band gap for the ordered ones. We speculate that another reason for the difference of the current collection might be a change in m^* and, accordingly, of the mobility.

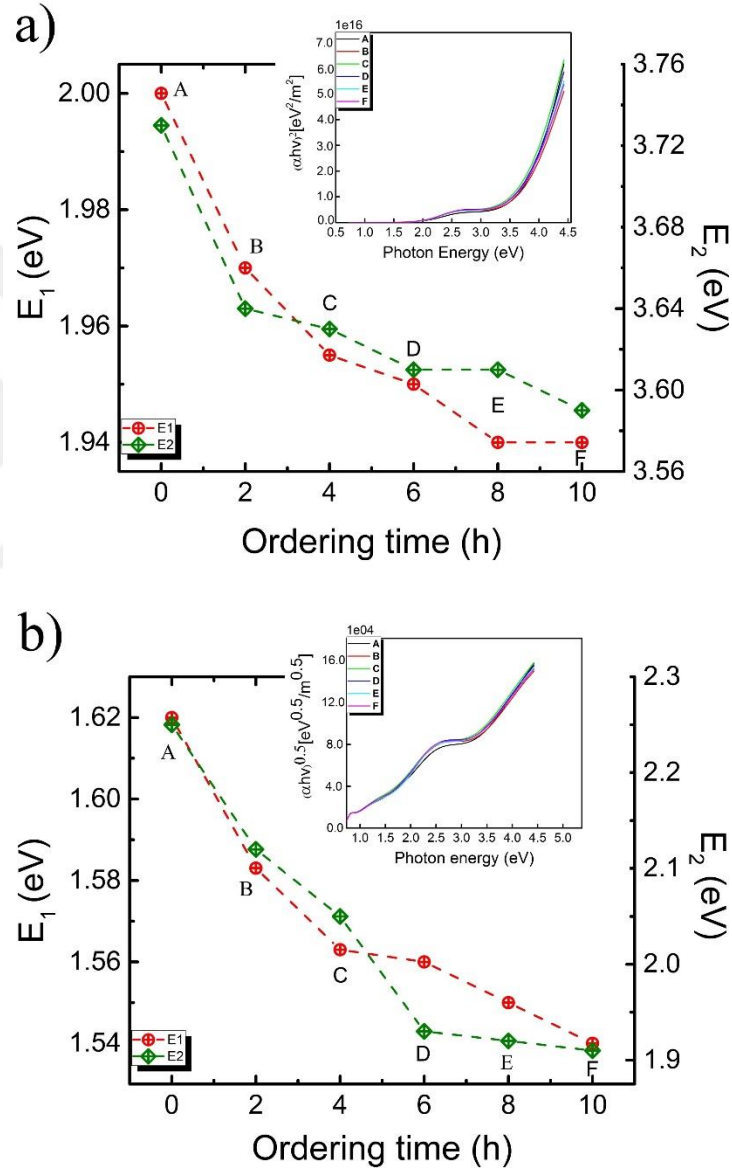


Fig.6. Further transitions E_1 (eV) and E_2 (eV) for different ordering states, inset: Tauc plots a) $(\alpha h\nu)^{0.5}$ versus $h\nu$ b) $(\alpha h\nu)^2$ versus $h\nu$ from SE data for each sample.

3.2 Raman Spectroscopy Results

Raman spectroscopy was performed for each sample state after each heat treatment step at 532 nm excitation wavelength. The average of five different measurement points was taken to exhibit a spectrum which is representative for the sample. Despite performing the Raman spectroscopy on each sample after

post-annealing, Fig. 7 illustrates the Raman spectra for only a minimum degree of ordered (A) and a maximum degree of ordered (F) samples for clarity.

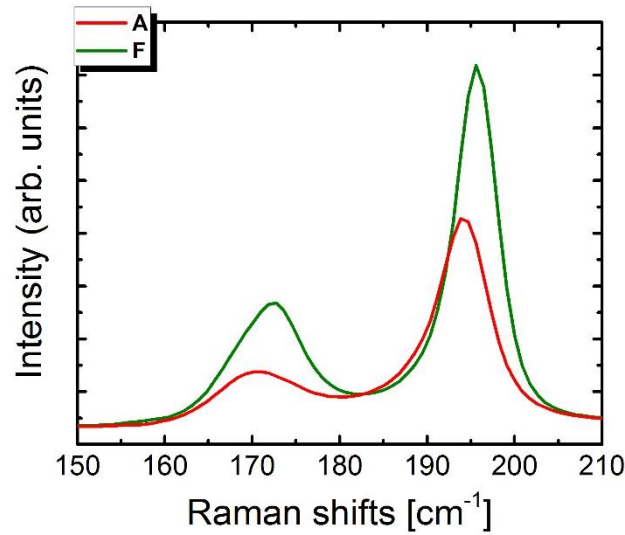


Fig. 7. Raman spectra of each sample at 532 nm excitation wavelength.

We observe that the main Raman peak becomes more narrow, shifts to a higher wavenumber, and the intensity increases with increasing ordering. Besides, three A-symmetry Raman modes are active in ordered CZTSe at 168 cm⁻¹, 174 cm⁻¹, and 196 cm⁻¹. Moreover, the disordered CZTSe sample has two active A-modes at 172 cm⁻¹ and 194 cm⁻¹ as expected from reported results [10,33]. Our findings are in fair agreement with other reports from literature [10,16,32,33], showing the effect of our heat treatment on the degree of ordering, as expected.

3.3 Photoluminescence Spectroscopy Results

PL spectroscopy was applied after each heat treatment step. However, Fig. 8 illustrates only two selected sample states, for clarity. We found the main PL peaks at 0.82 eV and 0.91 eV for the preferentially disordered state (sample A), and the highest degree of order (sample F), respectively. The values of the main PL peak are lower than the extracted band gap values E_0 from Spectroscopic Ellipsometry (SE), as it is usually observed in CZTSe due to band tailing and the defects [13,25,26]. However, the shift of the PL peak amounts to 90 meV.

We also observe that the PL peak shifts to the higher energy values (blue shift), and the main PL peak becomes broader with increasing ordering degree. These observations are in fair agreement with other reports [10,14,15].

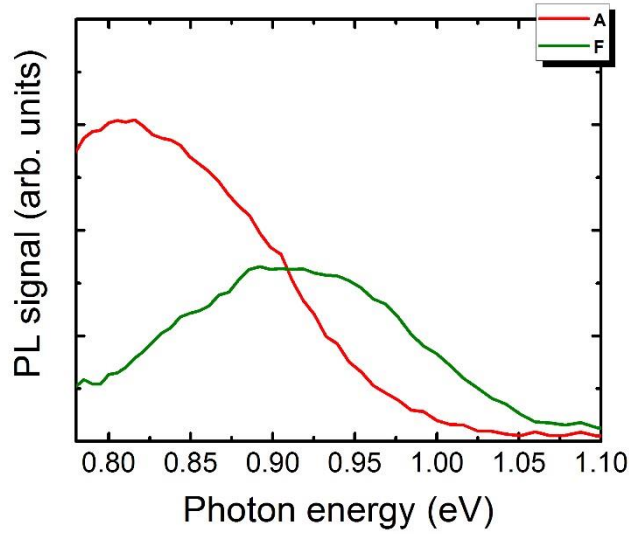


Fig. 8 PL spectra for only two selected post-annealing treatments: Minimum degrees of ordered sample A and the maximum degree of ordered sample F.

4. Conclusions

In this paper, we have investigated the effect of Cu-Zn disorder in CZTSe on the optical transitions by spectroscopic ellipsometry. We have found that Cu-Zn disorder causes a change not only in the first optical transition E_0 (fundamental band gap) but also in the further transitions E_1 and E_2 . While the absolute values of the first optical transition E_0 (from VBM to CBM at the Γ point) indicate an increasing trend with a higher degree of order, the absolute energy values of the further transitions E_1 and E_2 (from the VBM to CBM at Z point, and from VBM to uppermost conduction band at the Z point, respectively) show a decreasing trend with an increasing degree of order. These changes in band curvature of the bands in the $E(k)$ space probably may influence the transport properties of the CZTSe material including effective mass, mobility, etc, which should be investigated in detail in future studies, to understand the influence of Cu/Zn disorder on solar cell parameters.

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Chapter 7

7.1 Conclusion

In this thesis, it is shown that the thicknesses of the MoSe₂ sample and the CZTSe samples can be extracted from the SE data analysis. With a comprehensive optical model, it is possible to detect the secondary phases not only at the back side of the absorber but also at the front side of the absorber and within the absorber layer by SE. Therefore, the constructed optical model is critical to obtain the extensive results.

Additionally, the optical parameters such as refractive index and extinction coefficient for CZTSe samples were extracted to calculate the absorption coefficients, and then, to extrapolate the band gap values of CZTSe samples. Furthermore, SE was performed to investigate the interband structure of the CZTSe material which also shows the further transitions in CZTSe, i. e., critical points (CPs). For this purpose, a systematic study has been achieved by applying different heat procedure onto CZTSe absorber to investigate the effect of Cu-Zn disorder in CZTSe absorbers on optical transitions. It was found that Cu-Zn disorder causes a change not only in the first band gap E_0 (fundamental band gap) of the CZTSe but also in the further transitions E_1 and E_2 in the CZTSe absorbers. Moreover, it has been observed for the higher ordered CZTSe sample that while the first band gap E_0 reveals a blue shift, further transitions E_1 and E_2 show red shifts. The necessarily related change in band curvature may lead to a change in the transport property. Therefore, as a future recommendation, the role of disorder on the transport properties of the CZTSe material should be investigated to understand the mechanism and the effects of disorder on the solar cell parameters.

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Disclaimer

I hereby declare that this dissertation is my own original work and has not been submitted to before to any other institution for assessment purposes.

Further, I have acknowledged all sources used and have cited in the reference section.

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Özden Demircioğlu

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Date