Defect Engineering in Kesterite Materials for Thin Film Solar Cells

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Abstract

Cu$_2$ZnSnS$_4$ has great potential to be applied as an earth abundant and non-toxic absorber material in thin film solar cells, based on its suitable optical properties. However, several challenges have prevented the achievable efficiencies from exceeding 12.6 %, which is well below marketable efficiencies compared to competing solar cell technologies. One of the struggles in the development of Cu$_2$ZnSnS$_4$ solar cells is the high number of harmful defects leading to severe potential fluctuations. This thesis investigates different strategies of defect engineering in Cu$_2$ZnSnS$_4$, in particular to reduce Cu-Zn disorder.

Cu$_2$ZnSnS$_4$ thin films are produced by a two-step process, where Cu-Zn-Sn-S precursors are deposited by co-sputtering and then annealed at high temperature to yield crystalline films. The material properties are investigated with Raman spectroscopy, photoluminescence and spectrophotometry.

In the scope of this thesis, the following approaches to defect engineering are investigated: thermal treatments, varying partial pressures during the annealing step, and cation exchange to form the compound Cu$_2$MnSnS$_4$. Thermal treatments substantially enhance the degree of order in Cu$_2$ZnSnS$_4$. However, for the first time the severe limitations of such treatments are shown, indicating their insufficiency to reduce cation disorder to a level where potential fluctuations no longer affect Cu$_2$ZnSnS$_4$ solar cells. Furthermore, the stannite Cu$_2$MnSnS$_4$ suffers from cation disorder just like kesterite Cu$_2$ZnSnS$_4$ demonstrating that cation disorder is not restricted to the kesterite crystal structure and posing new challenges for finding new solar cell materials.

On the other hand, the presented results demonstrate a strong composition dependence of the ordering kinetics. Compositions with high densities of vacancies or interstitials significantly enhance the ordering rate by reducing the activation energy while the critical temperature is constant for the investigated compositions. Furthermore, the important effect of S$_2$ and SnS partial pressures during the annealing step of the fabrication is predicted from chemical models and experimentally verified by investigation of composition-spread Cu$_2$ZnSnS$_4$ thin films. Increasing both partial pressures leads to higher solubility of vacancies in Sn-rich Cu$_2$ZnSnS$_4$ further amplifying the positive effect of composition on the order-disorder transition. Investigation of composition-spread thin films further revealed the interplay between material properties and composition as well as secondary phases. In particular, the photoluminescence yield was drastically enhanced in the presence of SnS$_2$ secondary phases. This thesis discusses these results in the context of the current understanding of Cu$_2$ZnSnS$_4$.

Keywords: CZTS, thin film solar cells, defect engineering, composition-spread films, order disorder transition, intrinsic defects, secondary phases

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“Don’t let anyone rob you of your imagination, your creativity, or your curiosity. It’s your place in the world; it’s your life. Go on and do all you can with it, and make it the life you want to live.”

Mae Jemison
First female African American astronaut in space
This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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Author’s contributions

I Substantial contributions to the design of the experiment, sample fabrication, sample characterization and data collection, data analysis and interpretation, paper drafting and writing with input from co-authors.

II Substantial contributions to the design of the experiment, substantial contribution to sample characterization and data collection, data analysis and interpretation, paper drafting and writing with input from co-authors.

III Contributed to sample preparation (with thermal ordering treatments), supported analysis of Raman mapping and contributed to the discussion of the order parameter, input to manuscript writing.

IV Substantial contributions to experimental design, sample fabrication, sample characterization, experimental data analysis and interpretation, paper drafting and major part of writing with input from co-authors.

V Contributions to experimental design, supervision of a master thesis student, part of sample fabrication, part of sample characterization and data collection, data analysis and interpretation, paper drafting and writing with input from co-authors.
The following contributions were made during my studies, but are not included in this thesis:


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Sammanfattning på svenska

Styrning av defekter i kesteritmaterial för tunnfilms solceller


Idag dominerar solceller av kristallint kisel solcellsmarknaden. Produktionen av kiselsolceller kräver relativt stora mängder material och energi, detta på grund av att kisel inte absorberar ljus särskilt bra. Därför behöver kiselsolceller vara relativt tjocka vilket begränsar tillämpningarna och möjligheterna till kostnadsminskning i produktionen. Detta står i kontrast till tunnfilmsolceller som tack vare mycket god förmåga att absorbera ljus klarar sig med en tjocklek på mindre än en tiohals härstrå.

Det finns olika typer av tunnfilmssolceller. Det som skiljer dem åt är framför allt materialet som utgör det ljusabsorberande skiktet. Vissa typer av tunnfilmsolceller har verkningsgrader som liknar dem för solceller av kristallint kisel, framför allt de som består av Cu(In,Ga)Se2, ofta kallat CIGS, och CdTe. Både CIGS och CdTe-solceller tillverkas också kommersiellt. Dessa material är emellertid delvis gjorda av sällsynta eller giftiga ämnen, vilket gör produktionen dyrare, mer komplicerad och på sikt riskerar att begränsa mängden solceller som kan produceras.

Materialet Cu2ZnSnS4 (CZTS) består enbart av grundämnen som finns i stora mängder i jordskorpan och är inte giftigt. CZTS har ett direkt bandgap på ca 1.5 eV, vilket ger hög absorbtionskoefficient, dvs att det absorberar ljus väldigt bra. Därför har den stor potential att kunna användas som ett ljusabsorberande skikt i tunnfilmssolceller.

Den bästa verkningsgraden som uppnåtts för CZTS tunnfilmssolceller hittills är 12,6 %. Detta är emellertid fortfarande för lågt för att konkurrera med andra tunnfilmssolceller. Ett stort hinder för att nå bättre verkningsgrad är de många kristalldefekter som orsakar rekombination av laddningsbärarna innan de kan bidra till kretsen. Denna doktorsavhandling undersöker därför olika sätt att manipulera och kontrollera kristalldefekter i CZTS.

CZTS-proverna som undersöktes för denna avhandling framställdes genom så kallad samsputtring, där en substrat belades med tunna filmer bestående av
de fyra komponenterna koppar (Cu), zink (Zn), tenn (Sn) och svavel (S). I ett andra steg värmebehandlades de tunna filmerna i över 550 °C. Under denna process arrangerar atomerna sig i en periodisk struktur, ett så kallat kristallgitter. I fallet med CZTS har detta gitter kesteritstruktur, som kan härledas från diamantstrukturen.

Andra föreningar kan också bildas under värmebehandlingen, så kallade sekundärfaser, till exempel ZnS, CuS, SnS eller Cu₃SnS₃. Sekundärfaserna kan ha negativa effekter på solcellens prestanda. Den här avhandlingen visar att Cu₃SnS₄ har en särskilt negativ effekt på CZTS materialegenskaper, medan SnSₓ har en positiv effekt och minskar rekombinationsprocesserna i CZTS. I synnerhet måste de förhållanden som råder under värmebehandlingen kontrolleras mycket noggrant för att förhindra att CZTS sönderdelas till andra faser. I avhandlingen demonstreras att det är fördelaktigt att berika atmosfären under värmebehandlingen med S och SnS i gasform för att minimera avdunstning av dessa komponenter från CZTS-proven.

Den elektroniska bandstrukturen av ett material beskriver hur laddningsbärare (till exempel elektroner) kan röra sig i kristallen och bestämmer förmågan till ljusabsorption hos materialet. I en halvledare har bandstrukturen ett bandgap, dvs ett gap mellan de elektroniska banden och elektronerna kan inte befinna sig i det gapet. Det gör att ett material bara absorberar ljus med energi större än bandgapsenergin. CZTS absorberar emellertid en relativt stor mängd ljus i energiområdet under bandgapsenergin, vilket det inte borde. Detta indikerar att det finns många kristallfel materialet, som bildar energinivåer i bandgapet. Dessa energinivåer kan orsaka att rekombinationshastigheten ökar dramatiskt. När laddningsbärare rekombinerar betyder det att ledningsbärare förlorats innan de kan bidra till kretsen.


Dessutom kan förhållandena under värmebehandlingen justeras med höga partialtryck för SnS och S. Under dessa förhållanden ökar läsligheten för kopparvakanser i CZTS och fler vakanser kan bildas. Detta leder till en ytterligare förbättring av ordfningsfastheten under termiska behandlingar.

Ett annat sätt att minska Cu-Zn-oordningen är att ersätta ett av elementen. I detta arbete ersattes Zn av mangan (Mn), som inte är giftigt och förekommer i hög koncentration i jordskorpan. Föreningen Cu₂MnSnS₄ (CMTS) kristalliseras i stannitstrukturen, som är mycket lik kesteritstrukturen. Även om Cu och Mn skiller sig åt i storleken av kristallen och CMTS kristalliseras i en annan struktur än CZTS har det visats i den här avhandlingen att oordning av ato-
merna fortfarande finns i kvar i kristallen. Det förväntas därför att CMTS inte kommer att ge en förbättring för användning i solceller jämfört med CZTS. Baserat på kunskapen från avhandlingen kan rekommendationer härledas för vidare sökning efter framtida solcellsmaterial.
Zusammenfassung auf Deutsch

Defekt-Engineering in Kesterit-Materialien für Dünnschichtsolarzellen


Bisher wird ein Großteil der Solarzellen aus kristallinem Silizium hergestellt. Für die Herstellung von Silizium-Solarzellen ist ein großer Material- und Energieaufwand nötig, was die Möglichkeiten für Anwendungen und zur Kostenreduzierung in der Herstellung begrenzt. Dem gegenüber stehen Dünnfilmsolarzellen, welche mit einer kompletten Dicke von weniger als ein Zehntel vom Durchmesser eines Haares auskommen.

Technologien für Dünnfilmsolarzellen werden anhand des Materials unterschieden, welches die Absorbierschicht ausmacht. Einige dieser Technologien, zum Beispiel Cu(In,Ga)Se₂ (auch CIGS) oder CdTe basierte Solarzellen, haben Wirkungsgrade ähnlich dem von Silizium und werden bereits kommerziell hergestellt. Allerdings sind diese Materialien aus seltenen Erden oder giftigen Stoffen hergestellt, was die Herstellung komplizierter und teurer macht.

Das Material Cu₂ZnSnS₄ (CZTS) ist frei von seltenen Erden und ungiftig und hat zudem vorteilhafte Eigenschaften um als lichtabsorbierende Schicht (auch Absorber) in Dünnfilmsolarzellen angewendet zu werden. Es hat eine direkte Bandlücke mit einer Energie von etwa 1.5 eV, was zu einem hohen Absorptionskoeffizienten führt, das heißt, dass CZTS Licht sehr gut absorbieren kann. Auf der Basis von CZTS als Absorbermaterial wurden bisher Solarzellen mit bis zu 12.6 % Wirkungsgrad hergestellt. Dies ist allerdings noch zu wenig um mit anderen Dünnschichtsolarzellen konkurrieren zu können. Ein Hindernis für bessere Wirkungsgrade sind die vielen Gitterfehler, welche eine hohe Rekombinationsrate zur Folge haben. Rekombination der Ladungsträger bedeutet, dass diese verloren gehen, bevor sie zum Stromkreislauf beitragen können. Daher untersucht diese Doktorarbeit verschiedenen Möglichkeiten zur Manipulation und Kontrolle von Gitterfehlern in CZTS.

Die CZTS Proben, welche für diese Arbeit untersucht wurden, wurden durch Co-Sputtering hergestellt. Daraus resultieren Dünnfilme mit den vier
Bestandteilen Kupfer (Cu), Zink (Zn), Zinn (Sn) und Schwefel (S). In einem zweiten Schritt werden die Dünnfilme bei über 550 °C ausgeheizt. Dabei arrangieren sich die Atome in eine periodische Struktur, dem Kristallgitter. Im Fall von CZTS hat dieses Gitter die kesterite Kristallstruktur, welche sich aus der Diamantstruktur ableiten lässt.

Beim Ausheizen können sich auch andere Verbindungen bilden, so genannte Sekundärphasen, zum Beispiel ZnS, CuS, SnS, oder Cu2SnS3. Diese Sekundärphasen können negative Auswirkungen auf den Wirkungsgrad der Solarzelle haben. In dieser Arbeit wurde gezeigt, dass Cu3SnS4 sich besonders negativ auf die Materialeigenschaften von CZTS auswirkt, während SnSx eine positive Wirkung hat und die Rekombinationsrate in CZTS reduziert. Im Speziellen müssen die Bedingungen, die während des Ausheizens herrschen, genau kontrolliert werden, um den Zerfall von CZTS in Sekundärphasen zu unterbinden. Es ist zum Beispiel vorteilhaft die Atmosphäre während des Ausheizens mit gasförmigen S und SnS anzureichern, um Verdampfen dieser Komponenten von der Probe zu minimieren.

Die elektronische Bandstruktur eines Materials beschreibt, wie sich die Ladungsträger (zum Beispiel Elektronen) im Kristall bewegen können und bestimmt auch die Absorption eines Materials. In einem Halbleiter weist die Bandstruktur eine Bandlücke auf, also eine Lücke zwischen den energetischen Niveaus der elektronischen Bänder, in welcher sich die Elektronen nicht bewegen können. Das führt dazu, dass ein Material nur Licht mit höherer Energie als die Bandlückenergie absorbieren kann. CZTS absorbiert jedoch relativ viel Licht im Energiebereich unterhalb der Bandlückenergie, was darauf hinweist, dass viele Gitterdefekte (oder auch Gitterfehler) im Material vorhanden sind, welche zusätzliche Energieniveaus innerhalb der Bandlücke bilden. Diese Energieniveaus können die Rekombinationsrate gravierend anwachsen lassen und die Leistungsfähigkeit des Materials beeinträchtigen.

In dieser Doktorarbeit wurde gezeigt, dass die Rekombinationsrate in CZTS unabhängig von der Komposition sehr hoch ist. Der Rekombinationsgrad konnte nur durch die Präsenz der Sekundärphase SnS\textsubscript{x} verringert werden. Diese Beobachtung ist bersorgniserregend, da dies bedeutet, dass die Gitterfehler, welche zur Rekombination führen, nicht durch die Komposition von CZTS beeinflusst werden können.

Die Kupfer- und Zinkatome im CZTS-Kristall haben die selbe Größe als Gitterionen und es fällt ihnen dadurch leicht, ihre Kristallplätze zu vertauschen und Substitutionen zu bilden. Diese Gitterfehler kommen in CZTS so häufig vor, dass in typischen CZTS Proben Kupfer- und Zinkatome komplett ungeordnet auf den Gitterplätzen verteilt sind. Dies wird auch Cu-Zn-Unordnung genannt. Damit ist die Paarsubstitution Cu auf Zn (Cu\textsubscript{Zn}) und Zn auf Cu (Zn\textsubscript{Cu}) der bei weitem häufigste Gitterdefekt in CZTS. Da bei Cu-Zn-Unordnung beide Defekte zu gleichen Anteilen auftreten, ist Cu-Zn-Unordnung unabhängig von der Komposition.


Cu-Zn-Unordnung kann weiterhin durch andere Gitterdefekte beeinflusst werden, da diese Auswirkungen auf die Beweglichkeit der Cu und Zn Atome haben können und somit die Ordnungsrate verändern. Leerstellen oder Zwischengitteratome erleichtern die Substitution der Atome und fördern somit das “ordnen” der Cu und Zn Atome während einer Temperaturbehandlung. So kann der Effekt von Temperaturbehandlungen verstärkt werden und ein höherer Grad an Cu-Zn-Ordnung erreicht werden. Leerstellen und Zwischengitteratome finden sich vor allem in Cu-reichen und Cu-armen CZTS in Form
Zn-Zwischenatomen.


1. Introduction

Humanity currently faces its greatest challenge yet - tackling the unavoidable consequences of a human-caused, drastic change in the earth’s climate, and trying to shift from a lifestyle which is based on growth and consumerism, to a sustainable one taking the limits of our planet and consequences of our lifestyle on other living beings into consideration. A new generation led by the teenager Greta Thunberg is electrifying the whole world by the clear and inescapable message demanding immediate action to save their future. Meanwhile the older generation still in charge is struggling to find and implement suitable solutions, a latest example is the Green Deal initiated by the European Commission president Ursula von der Leyen with the vision to make Europe the first climate-neutral continent\(^1\). One of the key issues is to develop and implement sustainable, climate friendly ways to generate electricity for the worldwide growing demand. Solar cells play a central role in future scenarios for sustainable electricity generation.

The sun is a powerful energy source. The earth continuously receives a global mean surface radiation of \(185 \text{ W m}^{-2}\) from the sun\(^2\), or \(9.44 \times 10^6 \text{ GW}\) over the whole surface. A direct way to utilize this energy is through photovoltaic devices, i.e. solar cells, which can transform light energy directly into electricity.

Photovoltaics represents a clean and renewable source for electricity generation, and has been an active field of research for more than half a century. We have come a long way from the first silicon solar cell demonstrated by Bell laboratories in 1954 with 6% conversion efficiency\(^3\) to today, where multi-junction solar cells reach conversion efficiencies of up to 47.1%\(^4\). By the end of 2018, the worldwide cumulative installed photovoltaic capacity was 512 GW, providing 2.9% of the global electricity demand and the solar cell market has continued to grow rapidly\(^5\).

Beside being a green technology for electricity generation, solar cells yield several other unique advantages: Solar cells can be installed independent of the electric grid, and can provide electricity anywhere, where there is sunlight. Their electricity output is scalable, which presents the opportunity to adapt size of the installation to the demand and circumstances on-site. Furthermore, the cost of solar cell installations has decreased drastically over the last decades making them one of the cheapest electricity sources available (for installation in certain parts of the world) and reducing the payback time of solar cell installations below any other technology for electricity generation\(^6,7\).

The main challenge to integrate solar cell installations into the electric grid is that the output is fluctuating heavily from day to night time and due to
weather conditions. This presents the necessity for large scale energy storage to reduce the electricity output to the grid during times of peak production and to bridge periods of less solar irradiation. Unfortunately, there are still no large scale solutions to this challenge.

Up to now, the majority of the solar cells produced are based on crystalline silicon. Silicon is an abundant and cheap material and the industry for solar cell production has had a long time to evolve. However, due to the indirect band gap and poor absorption, thick layers of around 200 μm of silicon with high crystalline quality are necessary. This increases the production costs and constrains the applications of silicon solar cells. Thin film solar cells on the other hand rely on a thin stack of materials of only a few μm which allows the production of extremely light weight and even flexible solar modules. The reduction of the material allows decreasing production costs and faster pay back times. Materials used for thin film solar cells yielding competitive efficiencies are CdTe and Cu(In,Ga)Se₂ (CIGS). Unfortunately, these materials include rare and expensive or toxic elements which hinders their widespread application and up-scaling of the production to meet the growing energy demand. However, Kesterite Cu₂ZnSnS₄ (CZTS), which is studied in this thesis, could be a cheap and non-toxic alternative absorber material for thin film solar cell.

1.1 Kesterite for thin film photovoltaics

Kesterite Cu₂ZnSnS₄ (CZTS) has received considerable attention over the last 15 years as an alternative thin film absorber material, because it consists of abundant and non-toxic elements. CZTS has high absorption and a direct band gap at 1.5 eV, which can be tuned between 1.5 and 1.0 eV by partially replacing S with Se. Therefore, only a thin layer of 1–2 μm is sufficient for light absorption. It has been shown that CZTS thin films can be fabricated by several different deposition techniques including vacuum based processes yielding well performing solar cells.

The conversion of the energy of photons (i.e. of light) to an electric current is achieved through two main processes in the solar cell: (1) The photon is absorbed by the absorber layer of the solar cell which generates an electron in the conduction band and a hole in the valence band. (2) The electron and the hole are separated and collected by the contacts before they can recombine.

A typical stack of a CZTS solar cell is sketched in Figure 1.1 (a). The thickest layer of the solar cell stack is the CZTS absorber layer. As the name suggests, the absorber layer is the layer of the solar cell where (ideally) the majority of the photons are absorbed leading to the excitation of free electrons and holes, i.e. carrier generation. In order to collect the generated carriers from the absorber layer, an n-type buffer layer is introduced on top of the CZTS layer (in Figure 1.1 the buffer layer is made of CdS). The p-type CZTS
absorber layer and the n-type buffer layer form a pn-junction which leads to the formation of the space charge region at the interface and an internal electric field. The electrons and holes which are generated within the space charge region or which diffuse into the space charge region will be accelerated in opposite directions causing charge separation. The electrons are accelerated towards the buffer layer, while the holes are accelerated to the opposite direction, away from the buffer layer. The schematic band diagram of a CZTS solar cell and charge generation and separation is illustrated in Figure 1.1 (b). In CZTS solar cells the buffer layer is often formed by a CdS layer. However, based on the toxicity of CdS and the unfavorable cliff-like band alignment between CZTS and CdS (see Figure 1.1) alternative buffer layers could be an advantage. Therefore, CZTS solar cells with the alternative Cd-free buffer layers Zn(O,S)\textsuperscript{15} and Zn\textsubscript{1-x}Sn\textsubscript{x}O\textsubscript{y}\textsuperscript{16} have been demonstrated.

Finally, the carriers are collected by the front and back contacts. The metallic back contact collects the free holes and is usually made of molybdenum Mo. The electrons are collected by a transparent conducting oxide (TCO) layer, which is deposited on top of the buffer layer. Both the buffer and TCO layer should be as transparent as possible in order to reduce parasitic absorption. But at the same time they should also be good electron conductors. ZnO and Al doped ZnO are often used as TCO layers in CZTS solar cells. For solar cells produced in the lab, a narrow metal grid is often deposited on top to reduce the resistive losses in the TCO.

As other electrical devices, the performance of solar cells is most commonly analyzed by their current-voltage characteristics. Figure 1.2 shows the current-voltage curve (I-V curve) of a CZTS solar cell with a stack as described in Figure 1.1 (a). Without being illuminated, the I-V curve of a solar

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**Figure 1.1.** Structure of a solar cell with kesterite Cu\textsubscript{2}ZnSnS\textsubscript{2} as absorber layer. Sketch of band diagram and photovoltaic effect in the CZTS solar cell at short-circuit conditions ($V = 0$).
cell resembles the exponential behavior of a pn-junction. Under illumination, the I-V curve is shifted along the current axis by the amount of the light current $I_L$. Therefore, the I-V characteristics of an ideal solar cell under illumination can be described by the adapted ideal diode equation \(^{17}\)

$$I(V) = I_0 \left[ \exp \left( \frac{qV}{nk_B T} \right) - 1 \right] - I_L . \quad (1.1)$$

$I_0$ is the reverse saturation current which is driven by recombination, $q$ is the elemental charge, $n$ is the ideality factor, $k_B$ is the Boltzmann constant and $T$ is the temperature. It should be noted that the current $I$ is often expressed as current density with the formula sign $J$ in A/m\(^2\) to remove the dependence on the cell area. The ideal diode equation and Equation 1.1 do not accurately describe the I-V characteristics of real solar cells, as the one shown in Figure 1.2. That is because equation 1.1 does not consider resistive effects, and the so called cross-over where the IV-curve under illumination crosses the IV-curve without illumination cannot be explained with Equation 1.1.

The I-V curve of a solar cell is characterized by two distinct points: the open circuit voltage $V_{OC}$, the voltage that builds up when no current flows between the contacts, and the short circuit current $I_{SC}$, the current at zero voltage. Furthermore, the maximum power point along the curve is found where the product $V \cdot I$ is largest. The fill factor can then be defined by the ratio

$$FF = \frac{V_{mp} \cdot I_{mp}}{V_{OC} \cdot I_{SC}} . \quad (1.2)$$
Finally the conversion efficiency $\eta$ can be defined by the parameters extracted from the I-V curve

$$\eta = \frac{V_{OC} \cdot I_{SC} \cdot FF}{P_{in}}, \tag{1.3}$$

where $P_{in}$ is the power input, in case of a solar cell this is the power of the illuminating light$^{17}$.

From equation 1.3, the three parameters $V_{OC}$, $I_{SC}$ and $FF$ should be as high as possible to maximize the conversion efficiency of the solar cell. According to equation 1.1, the short circuit current $I_{SC}(V = 0)$ should be equal to the light current $I_L$ for an ideal solar cell. It becomes clear, that any effect reducing the light absorbed in the absorber layer, e.g. reflection or parasitic absorption in the buffer layer, reduces $I_L$ and has a negative effect on $I_{SC}$.

An important property defining the absorption in the absorber layer is the band gap of the absorber material. A small band gap increases the range of photons that can be absorbed, because photons with photon energy smaller than the band gap are insufficient to excite electrons to the conduction band. Therefore, a smaller band gap $E_G$ is preferable with respect to the short circuit current $I_{SC}$. On the other hand, after charge generation all energy transferred from the photon to the electron greater than $E_G$ will be lost due to thermalization. Therefore, $E_G$ is directly related to the achievable output voltage $V_{OC}$ and higher $E_G$ will improve $V_{OC}$. This conflicting dependence of $V_{OC}$ and $I_{SC}$ leads to an optimal range of the band gap between 1.1 eV and 1.6 eV for the absorber material in single junction solar cells, where the maximum achievable efficiency is around 30%$^{18}$ (also known as Shockley-Queisser limit). The band gap of CZTS with $E_G = 1.5 – 1.6$ eV falls within this range and is therefore a suitable semiconductor for photovoltaic applications.

An expression for $V_{OC}$ can be derived from equation 1.1 by applying $I = 0$, which gives

$$V_{OC} = \frac{k_B T}{q} \ln \left( \frac{I_L}{I_0} + 1 \right). \tag{1.4}$$

A higher light current $I_L$ has a positive effect on $V_{OC}$, while the reverse saturation current $I_0$ should be as small as possible to maximize $V_{OC}$. Because $I_0$ is proportional to the recombination in the solar cell, $V_{OC}$ is heavily affected for example by defects acting as recombination centers. The shortcoming of $V_{OC}$ is often expressed as a function of $E_G$ as the open circuit voltage deficit $\Delta V_{OC}$

$$\Delta V_{OC} = \frac{E_G}{q} - V_{OC}. \tag{1.5}$$

In CZTS solar cells the large $V_{OC}$ deficit is most troublesome. Record efficiencies of solar cells based on Cu$_2$ZnSn(S,Se)$_4$ have stagnated at 12.6%$^{14,19}$ and fall behind other thin film solar cells like CdTe, CIGS and perovskite technologies. Several bottle necks have been identified that are likely to limit the conversion efficiency in CZTS solar cells: (1) Sulfurization of Mo at the
metallic back contact leads to the formation of MoS$_2$ and to decomposition of CZTS into secondary phases causing a higher series resistance and increased recombination at the back interface. (2) the unfavorable band alignment between CdS and CZTS forming a so-called cliff band alignment at the interface (see also Figure 1.1 (b)). This causes interface recombination and $V_{OC}$ losses. The alternative buffer layers Zn(O,S)$^{15}$ and Zn$_{1-x}$Sn$_x$O$_y$$^{16}$ seem to solve this problem in CZTS solar cells. However, the absence of a major improvement of the solar cell performance leads to the suspicion that other shortcomings still remain.

Which leads to bottleneck number (3): the high intrinsic defect densities in the bulk CZTS absorber layer present a serious challenge on the path towards improving CZTS solar cell conversion efficiencies. The problems in the CZTS bulk have been identified as the main impediment to increasing the device efficiency of CZTS solar cells. The intrinsic defects and defect complexes cause detrimental band tailing and potential fluctuations which cause CZTS to suffer from a high rate of recombination limiting the $V_{OC}$.$^{23,24}$ This issue has been broached in numerous studies.$^{25,26,27}$ However, so far no solution towards higher efficiencies has been found. Cu-Zn disorder and deep defects, such as Sn$_{Zn}$, have been identified that could potentially lead to such a detrimental effect on the material properties.

1.2 Scope and aim of this thesis

The research presented in this thesis attempts to address the final challenge presented in Section 1.1: the intrinsic defects and crystalline quality of CZTS. When the work for this thesis started in January 2015, it was widely accepted in the research community that CZTS crystallizes in the kesterite crystal structure with abundant Cu-Zn disorder.$^{28}$ Detrimental potential fluctuations had been identified as a possible limitation of $V_{OC}$ and characterization of the intrinsic defects as well as Cu-Zn disorder was a hot topic.$^{29,30,31}$ Achieving control over the defects and their effect on a material is referred to as “defect engineering”. In this work, different possibilities for defect engineering in CZTS are explored in order to control the nature of the defects with the aim to improve the properties of the CZTS material. A special focus is placed on the reduction of Cu-Zn disorder in CZTS. The strategies investigated in particular involve

1. Temperature treatments to reduce disorder (Paper I)
2. Composition tuning for fast ordering kinetics (Paper II)
3. Tuning the annealing step in the fabrication process to find ways to influence the composition and the nature of intrinsic defects (Paper III and V)
4. Cation exchange to form related materials to explore the possibility of avoiding cation disorder (Paper IV).
The following chapters present the results of these works in the wider context of the current understanding of CZTS as a solar cell absorber material. The thesis is arranged in four chapters covering the structure of CZTS in Chapter 2, and defects and electronic properties of CZTS in Chapter 3. The cation disorder as the most abundant defect in CZTS is discussed in detail in Chapter 4. Finally possibilities for defect engineering in CZTS are elaborated in Chapter 5 with a focus on the results from Papers I to V. The thesis is completed by Chapter 6 which summarizes the main conclusions and presents an outlook from this work.
2. Structural properties

The crystalline structure of a solid is defined based on the atoms that it is build from, e. g. their size and the occupation of the electron shells. For each combination of atoms, there is one preferred structure in which the atoms align. This crystal structure in turn defines essential properties of the solid, such as the electronic band structure. This chapter describes the structural properties of Cu2ZnSnS4 (CZTS) and the fabrication methods exploited in this thesis for CZTS thin film fabrication. The fabrication of this quaternary compound implicates some new challenges with regard to decomposition based on the volatility of Sn and SnS at high temperatures. Therefore, the chapter also covers different models describing the decomposition of CZTS and segregation of secondary phases and their effect on devices and on the CZTS material properties are discussed.

2.1 The CZTS crystal

As depicted in Figure 2.1, the Cu2ZnSnS4 lattice can be derived from the zincblende ZnS lattice by aligning a Zn, a Sn and two Cu atoms on the cation sites around one S atom forming S-Cu2ZnSn tetrahedral motifs that satisfy the octet rule. Several polymorphs can be constructed from these tetrahedra including the stannite (space group I42m), kesterite (I4), the PCMA structure (primitive-mixed CuAu structure with space group P42m) and another tetragonal structure with space group P42c. First principles Density functional theory (DFT) calculations predicted the kesterite structure to be the most stable crystal structure33,34. The kesterite ground state structure of CZTS could be confirmed with neutron diffraction experiments35. The kesterite phase is stable up to 876 °C where a phase transition to cubic sphalerite structure (space group F43m) occurs28. Experiments by neutron diffraction further gave evidence for disorder in the Cu-Zn planes of the kesterite structure (for more information about Cu-Zn disorder see Chapter 4). The other two tetragonal polymorphs of CZTS with space group P42m and P42c can be formed under certain fabrication conditions and can be differentiated from the kesterite structure by Raman spectroscopy36 (see Box 2.1).

2.2 Fabrication of thin film CZTS

Fabrication of CZTS thin films with good crystallinity faces several challenges. On one hand, crystallization of CZTS requires temperatures of 500 °C
Figure 2.1. Comparison of CZTS with kesterite and stannite crystal structure, which can both be derived from the zincblende structure of ZnS. Both kesterite and stannite CZTS are built from \(S-Cu_2ZnSn\) tetrahedral motifs. Produced with the Software CrystalMaker.\(^{32}\)

or higher\(^{37,38}\). On the other hand, SnS phases become highly volatile at such high temperatures which drives the decomposition of CZTS\(^{39}\), as is discussed in detail in Section 2.3. This makes it difficult to implement a single-step process for fabrication. There have been few approaches to produce CZTS thin films by co-evaporation\(^{40,41}\) and sputtering\(^{42}\) in a single step. However, the general route to produce CZTS thin films involves a two-step process. In the first step, a precursor containing Cu, Zn, Sn, and S is deposited at rather low temperatures and during the second step the precursor is annealed at a higher temperature in a controlled environment to reduce evaporation of SnS. Various techniques have been employed for the precursor deposition ranging from vacuum techniques, such as sputtering\(^{43,19,44}\) and evaporation\(^{45}\), to solution-based processing\(^{14,46}\).

The precursors for the samples investigated in Papers I to V were produced by co-sputtering from alloy and metal targets (either CuS, Zn, and Sn, in active mode with \(H_2S\), or CuS, ZnS and SnS). The substrates were soda-lime glass covered by DC-sputtered molybdenum to resemble the processing of solar cell fabrication where a molybdenum layer is used as the back contact. In the cases where a transparent substrate was needed for characterization (Paper IV), the precursors were directly deposited on the soda-lime glass. Soda-lime glass is not only a cheap and heat durable choice for the substrate, but it also contains sodium (Na) which out-diffuses into the Cu-Zn-Sn-S layer during the annealing step and substantially improves crystallization\(^{47}\). During deposition of the precursors the substrate holder was heated to 250 °C. The substrate holder is usually rotated to achieve uniform composition across the sample area. In Papers II, III and V the Cu-Zn-Sn-S precursors were deposited without substrate
Box 2.1: Raman spectroscopy

Raman spectroscopy measures the spectrum of lattice vibrations of a material, also called phonons. Lattice vibrations depend on the mass of the vibrating atoms and the characteristics of the bonds to their neighboring atoms, e.g. bond lengths and strength. This leads to a characteristic set of phonon modes for every material and enables phase identification based on Raman spectra.

The principle of Raman spectroscopy is illustrated in the Figure: 1. An incoming photon excites an electron. 2. The electron scatters with the lattice, which creates (annihilates) a phonon. 3. The electron recombines emitting a photon with an energy lower (higher) than the incoming photon $\Delta E$ equal to the created (annihilated) phonon energy. The phonon spectrum is acquired by measuring the energy difference $\Delta E$. Therefore it is important to use a monochromatic light source, typically a laser, as excitation source.

In order to stimulate photon-electron interaction, the incoming photons must have an energy equal or higher than the band gap of the material. Resonant Raman conditions apply if the energy of the incoming photon is close to the band gap energy or another optical transition energy. Then the photon-electron interaction probability is greatly enhanced which leads to higher intensity of the Raman spectrum.
Box 2.2: Composition measurements

Energy-dispersive X-ray spectroscopy (EDS or EDX) and X-ray fluorescence spectroscopy (XRF) utilize the characteristic X-ray emission to quantify the elemental composition of a sample. EDX uses an electron beam as excitation source. Because of the high interaction probability of electrons with matter, the probing volume is rather small which leads to a low probing depth and uncertainties in the resulting atomic composition of about \( \pm 5\% \). XRF on the other hand relies on high energy X-rays as excitation source, which provides a deep probing depth and more accurate compositions. However, the setup needs to be calibrated by a sample with known composition. For the composition studies of this thesis, the calibration sample for XRF was analyzed by Rutherford back scattering (RBS) which is an ion beam technique. This technique delivers rather exact composition results but requires an elaborate experimental setup.

rotation which led to a continuous gradient in the cation composition across the sample area. These samples are referred to as composition-spread CZTS thin films. The precursors deposited by co-sputtering from alloy targets were fully sulfurized and featured a poorly crystalline structure of the zincblende type with small grains\(^48\).

A crucial aspect during the precursor deposition is the control of the cation composition, because the composition of the precursor impacts the secondary phase formation and the nature of the defects in the final CZTS film. In general, the integral composition of the Cu-Zn-Sn-S precursor films was measured by X-ray fluorescence using a calibration sample that had been characterized by Rutherford back scattering\(^49\). The composition of composition-spread CZTS films was mapped with energy dispersive X-ray spectroscopy (see Box 2.2).

In the second processing step, the precursors were annealed in a tube furnace to enhance the crystallinity and grain growth. The samples were placed in a graphite box together with elemental sulfur (or other sulfur and SnS sources in Papers III and V). Argon served as an inert process gas in the tube furnace. The graphite box was inserted from a cold loading zone into a pre-heated hot zone and removed after the annealing time which ranged from 2 min to 13 min. The annealing temperature was around 550-580 °C. The small volume in the graphite box together with the short annealing times allowed to sustain a sulfur rich atmosphere for the duration of the high temperature anneal and by that reduce sulfur and SnS loss from the sample by evaporation. Nevertheless, a composition shift is typically observed when comparing the annealed CZTS film with the precursor film due to Sn-loss. The mechanisms of Sn-loss during the high temperature anneal will be discussed in Section 2.3.
The annealing step needs to be carefully optimized in order to yield CZTS thin films of high quality. Because the annealing process in the tube furnace is a non-equilibrium process, there is a trade-off between long annealing time, yielding larger grains, and maintaining the sulfur and SnS partial pressures, which degrade for longer annealing times. Other parameters that need to be optimized are the annealing temperature and the tendency of the CZTS film to peel off based on residual stresses from sputtering and on stress and strain exerted on the film and the substrate under fast temperature changes.

Prior to further deposition, the surface of the CZTS film is conditioned by KCN etching to remove oxides, sulfates and some of the secondary phases from the CZTS surface. For the complete stack of a solar cell, the transparent ‘window’ layers are deposited on top of the (etched) CZTS absorber layer. A common buffer layer to form the pn-junction with Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) is cadmium sulfide CdS which is deposited by chemical bath deposition. However, CdS does not form an optimal band alignment with CZTS and is often criticized for its toxicity. Therefore, alternative buffer layers have been investigated, yielding promising candidates such as Zn(O,S) and Zn$_{1-x}$Sn$_x$O$_y$. The front contact is then completed with an intrinsic ZnO layer and an Al-doped ZnO layer and in some cases a metal grid for reduced resistivity losses. The complete stack of a CZTS solar cell is illustrated in Figure 1.1 (a).

2.3 Models for phase stability and decomposition into secondary phases

A reoccurring challenge in the fabrication of CZTS thin films is to avoid secondary phase formation, because they can have a detrimental impact on the device performance of solar cells. Common secondary phases in CZTS thin films are shown in the ternary phase diagram in Figure 2.2 and their effect on solar cell characteristics according to are listed in Table 2.1. The best devices are fabricated with Zn-rich CZTS in order to avoid formation of the detrimental phases Cu$_x$S and Cu$_2$SnS$_3$. It should be noted that Figure 2.2 represents the equilibrium state of the quaternary Cu-Zn-Sn-S system at 400 °C. The phase diagram is expected to differ for conditions that apply during thin film fabrication. This explains why other secondary phases are commonly observed in CZTS thin films as well, such as SnS, or Cu$_3$SnS$_4$ which is observed in composition-spread CZTS thin films.

Secondary phases can form directly from the precursor during the growth, which is considered segregation of secondary phases, or they can form when CZTS decomposes into ternary or binary phases. Several reasons have been identified that facilitate secondary phase formation during the growth of CZTS. Even though kesterite Cu$_2$ZnSnS$_4$ is the stable phase for the quaternary system Cu-Zn-Sn-S, its phase stability region is rather narrow according to
Figure 2.2. Sketch of the ternary phase diagram at 400 °C, according to Ref. 54. Only discussed secondary phases are included. Some secondary phases, such as Cu₃SnS₄, CuS and SnS are not shown, as they do not lie in the same plane due to their S content.

Table 2.1. Typical secondary phases observed in Cu₂ZnSnS₄ thin films and their effect on solar cell characteristics according to Ref. 55.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Property of phase</th>
<th>Effect on device</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>$E_g = 3.6 \text{ eV}$</td>
<td>reduces effective area, can increase series resistance</td>
</tr>
<tr>
<td>CuₓS</td>
<td>$1.2 \text{ eV} &lt; E_g &lt; 2.5 \text{ eV}$, highly conductive/metallic</td>
<td>severe shunting, recombination reduces $V_{OC}$</td>
</tr>
<tr>
<td>SnSₓ</td>
<td>$1.1-2.2 \text{ E}_g$</td>
<td>barriers for carrier collection</td>
</tr>
<tr>
<td>Cu₂SnS₃</td>
<td>$0.98-1.35 \text{ E}_g$</td>
<td>recombination and lower $V_{OC}$, reduced carrier collection</td>
</tr>
</tbody>
</table>
theoretical investigations, i.e. it cannot tolerate large deviations from the stoichiometric 2:1:1:4 atom ratios without precipitation of secondary phases. To prevent segregation of CuS, SnS or SnS₂, ZnS and Cu₂SnS₃ the processing conditions, including the composition, need to be carefully adjusted. Even small deviations can lead to secondary phase formation and it is not unusual that several secondary phases are observed together in the same sample along with the kesterite CZTS phase.

Decomposition of CZTS into the binaries is driven by the instability of Sn(IV) in CZTS at high temperatures and low S₂ partial pressure. Reaction 2.1 depicts the decomposition of CZTS into its binary secondary phases leading to the reduction of Sn(IV) in CZTS to Sn(II) in SnS. The high vapor pressure of SnS then drives Reaction 2.2 where SnS evaporates by forming gaseous SnS.

\[
\begin{align*}
\text{Cu}_2\text{ZnSn(IV)}\text{S}_4(s) & \rightleftharpoons \text{Cu}_2\text{S(s)} + \text{ZnS(s)} + \text{Sn(II)S(s)} + \frac{1}{2} \text{S}_2(g) \quad (2.1) \\
\text{SnS(s)} & \rightleftharpoons \text{SnS(g)} \quad (2.2)
\end{align*}
\]

These reactions represent equilibria, i.e. they are reversible and expected to occur in both directions simultaneously. The rate at which the reaction and its reverse reaction occur and the ratio of the products of the system in equilibrium are determined by the boundary conditions of the system. Therefore, the decomposition described in Reactions 2.1 and 2.2 can be prevented by ensuring sufficient S₂ and SnS partial pressures. This will limit SnS loss and decomposition of CZTS which can have a detrimental effect on the solar cell performance.

One reaction initiating the decomposition of CZTS into its secondary phases arises from the sulfurization of the molybdenum back contact which occurs during the high temperature anneal. Typically, a MoS₂ layer of a few hundred nm is formed at the back contact. The formation of MoS₂ is not only problematic based on the negative impact on the series resistance of CZTS solar cells, but also because it leads to sulfur deficiency in the CZTS layer causing decomposition of CZTS into its binary secondary phases.

\[
2\text{Cu}_2\text{ZnSn(IV)S}_4 + \text{Mo} \rightarrow 2\text{Cu}_2\text{S} + 2\text{ZnS} + 2\text{Sn(II)S} + \text{MoS}_2 \quad (2.3)
\]

Another approach to understand the phase stability of CZTS is given in Paper III, where a chemical model for the single phase region is established based on equilibria of the defect complexes that are formed in the off-stoichiometric CZTS phase (see also Section 3.3). The single phase region encompasses the composition range where CZTS is formed without secondary phase segregation. This region should contain the point of stoichiometric composition. For any other point in the single phase region, the off-stoichiometric composition implies the formation of defect complexes and the density of these defect complexes increases further away from the stoichiometric point (defect complexes in CZTS are discussed further in Section 3.3). At a certain composition...
the formation of defect complexes will be less favorable than segregation of secondary phases. Therefore the edge of the single phase region marks the solubility range of the defect complexes in that composition range. The solubility of the defect complexes is not constant for the material, but changes with temperature and processing conditions, such as partial pressure of $S_2$ and SnS. Hence, in this model the equilibrium is formed between CZTS containing a defect complex and CZTS with secondary phases. For example, for the B-type defect complex $(2ZnCu + ZnSn)$ the equilibrium reaction is

$$2Cu_2ZnSnS_4 \text{ with } (2ZnCu + ZnSn) \rightleftharpoons Cu_2ZnSnS_4 + 4ZnS . \quad (2.4)$$

The equilibria involving other defect complexes and secondary phases can be derived similarly.

Equilibria involving SnS$_2$ as a segregated secondary phase will again be affected by the SnS and $S_2$ partial pressures based on the reaction

$$\text{SnS}_2(s) \rightleftharpoons \text{SnS}(g/s) + \frac{1}{2}S_2(g) , \quad (2.5)$$

and the solubility of these defect complexes will depend heavily on the processing conditions. The conclusion regarding solubility limits of defect complexes in CZTS is that not only the composition of the precursors determines the nature of the intrinsic defects, but also the fabrication conditions with regards to $S_2$ and SnS partial pressures.

These results explain, why phase segregation occurs even if the integral composition is inside the (equilibrium) phase region illustrated in Figure 2.2. During processing of CZTS thin films for solar cell applications, we should instead consider the non-equilibrium single phase region including the implications on secondary phase segregation and solubility of intrinsic defect.

2.4 Experimental investigation of the single phase region

Previous experimental investigations of the phase stability of CZTS in terms of composition and the extent of the single phase region are based on single crystal and powder samples fabricated by solid state reaction$^{29,62,63}$. Based on the different processing conditions compared to thin film fabrication techniques, these findings are not expected to match the situation of thin film processing very well. In Papers III and V a different approach is presented to study the phase stability and the single phase region of CZTS under thin film processing conditions using composition-spread CZTS thin films (see Box 2.3). In Paper III, this method was applied to validate the model of the phase stability based on the solubility of defect complexes.

In order to identify the single phase region on the composition-spread samples, the secondary phase boundaries (boundary marking the region where
Box 2.3: Investigation of composition-spread CZTS samples

In Papers III and V an experimental approach has been established to identify the single phase region of CZTS composition-spread samples combining X-ray diffraction and Raman spectroscopy for secondary phase analysis. With the known composition boundaries for secondary phase formation, it is possible to distinguish effects of secondary phases from effects of composition changes in CZTS. This knowledge is vital for understanding the potential for defect engineering because the formation energy of defects depends on the chemical potential which is again tied to the composition.

The approach to use composition-spread samples presents the opportunity to study the phase stability region of CZTS under thin film processing conditions. This would be impossible by means of individually produced CZTS films without composition-spread, but each with a slightly different composition to cover the full single phase region in compositions (or at most very tedious to realize as an experiment and to interpret the results). By the approach of using composition-spread samples, it is secured that the full composition range is exposed to the exact same fabrication process in terms of sputtering, annealing and temperature history, but also rest times in between processing steps. However, this approach also comes with some challenges, such as handling and interpretation of the huge amount of data from mapping the sample area by different analysis techniques. Furthermore, it is undeniable that the processing conditions of composition-spread CZTS do lead to some differences in phase formation in the ternary Cu-Sn-S secondary phases: typical Zn-poor CZTS thin films exhibit the ternary phase Cu₂SnS₃. For composition-spread CZTS films on the other hand, segregation of Cu₃SnS₄ is observed (see and Papers III and V). This difference could be caused by the interactions of the different composition regions via the gas phase.
X-ray diffraction (XRD) is a common technique to study the crystal structure of a material. A monochromatic X-ray beam (typically the Kα radiation of Cu with $\lambda = 1.5406$ Å) is elastically scattered by the electrons of the atoms in the crystal. At certain angles $\theta$ to the incoming beam, the scattered x-rays interfere constructively according to Bragg’s law

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

and the diffraction pattern will feature a peak at that angle. From the angles $\theta$ of constructive interference the distance $d$ between the crystal planes can be calculated.

For the analysis of thin films, the incoming beam can be fixed at a very low angle, typically between 0.5° − 2°, to increase the probed volume. This technique is called Grazing incidence X-ray diffraction or GI-XRD. It is important that the films are polycrystalline and non-oriented to ensure that all diffraction peaks of the pattern are recorded.

In Papers III and V X-ray diffraction (XRD, see Box 2.4) was used to identify Sn-S related secondary phases and to find their phase boundaries. However, the diffraction pattern of Cu$_2$ZnSnS$_4$ overlaps with other binary and ternary sulfides based on the similarities in their structure. Therefore, XRD is unsuited to identify the secondary phases ZnS and Cu$_3$SnS$_4$. Additionally, the identification of CuS proved to be difficult by XRD. Instead, the secondary phases ZnS, CuS and Cu$_3$SnS$_4$ were analyzed by multiwavelength Raman spectroscopy which was shown to be a suited complementary technique to XRD for secondary phase identification$^{65,66}$. For multiwavelength Raman spectroscopy, the Raman spectrum is recorded under different excitation wavelengths that match optical transitions of potential (secondary) phases of the sample in order to measure their response in resonant condition. This way the Raman signal of even small amounts of a phase can be detected.

XRD can scan the full sample stack including the Mo back contact. Raman spectroscopy on the other hand is a surface-sensitive technique and secondary phases that occur deeper within the film are more difficult to detect, while the Raman response from secondary phases close to the surface may be enhanced. In Paper V the secondary phase assignment was therefore cross-checked with combined scanning transmission electron microscopy and energy dispersive X-ray spectroscopy (STEM-EDX).

Figure 2.3 shows the outline of a composition-spread CZTS thin film in a composition diagram. The secondary phase boundaries from XRD and Raman...
Figure 2.3. Composition region covered by a composition-spread CZTS sample with secondary phase boundaries indicated by white dotted and dashed lines. The single phase region is marked with a white star.

mapping are indicated by white dotted and dashed lines. The region enclosed by these boundaries represents the CZTS single phase region. With the outline of the single phase region established, the properties of the CZTS phase within this region are investigated in Papers III and V by studying the Raman characteristics. These yield information about the crystalline quality of the material and about defects present in CZTS, in particular the \( Q \) parameter which can be extracted from resonant Raman spectra of CZTS\(^6\) (see Chapter 4 for more information about \( Q \)).

The trends observed for the \( Q \) parameter across the composition-spread sample are discussed in more detail in Section 5.1 and Figure 5.2 shows the \( Q \) parameter for two composition-spread CZTS films annealed under different conditions. In Paper III these trends are used to confirm the model describing the stability of the single phase region based on the solubility of defect complexes which was described in the previous section. The \( Q \) parameter reflects the expected trends for defects in off-stoichiometric CZTS: within the single phase region the density of defects increases away from the stoichiometric composition and stagnates at the composition where secondary phases appear. In other words, the boundary of the single phase region marks the solubility limit of certain defects in the CZTS crystal. In regions that are outside the single phase region, the density of defects remains almost constant. Instead of implementing more defect complexes in the CZTS phase, secondary phases are formed. Therefore, segregation of secondary phases can be regarded as a consequence of limited solubility of defects in the CZTS phase. The effect of
defects on the properties of the CZTS phase will be further discussed in the following chapters of this thesis.

The areas of the composition-spread sample outside the single phase region yield information about the interplay of the CZTS phase and the secondary phases. Paper V discusses the effect of secondary phases on CZTS based on observations from Raman spectra and photoluminescence (see Box 3.2). Figure 3.4 shows the photoluminescence intensity across two composition spread samples annealed under different conditions. Comparing the trends across the samples with the outline of the secondary phase boundaries reveals that ZnS and Cu$_x$S do not influence the photoluminescence intensity. However, the ternary phase Cu$_3$SnS$_4$ severely reduces the photoluminescence intensity. A similar, detrimental effect of this phase can be observed on features of the Raman spectrum (see Figure 5.2). In Paper V it is proposed that Cu$_2$ZnSnS$_4$ and Cu$_3$SnS$_4$ form a solid solution. The presence of Sn-S phases on the other hand enhances the photoluminescence intensity by several orders of magnitude.

Figure 2.4 shows scanning transmission electron microscopy cross section images extracted from different positions across the composition-spread samples. The cross section images reveal that the morphology of the CZTS film is enhanced for Sn-rich compositions of the composition-spread CZTS films compared to stoichiometric or Zn-rich regions. Sn-rich CZTS exhibits larger grains and a reduced number of visible extended defects (i.e. stacking faults or dislocations). However, it is unclear whether the enhanced morphology is caused by the presence of SnS$_x$ phases or by the Sn-rich composition of the CZTS phase.

The exact origin and mechanisms behind the interplay of the SnS$_x$ secondary phases and the CZTS phase leading to higher photoluminescence intensity and possibly enhanced morphology and grain growth are not understood. Some possibilities are discussed in Paper V, e.g. passivation of inter-

*Figure 2.4. Cross section images of a composition-spread CZTS thin film at different compositions. The images were acquired by scanning transmission electron microscopy. Adapted from Paper V.*
faces by SnS$_x$ phases, the effect of secondary phases on the growth mechanisms and inhibited decomposition of CZTS based on the presence of SnS$_x$ phases.

This chapter summarizes the challenges in the fabrication of Cu$_2$ZnSnS$_4$ thin films connected to decomposition and segregation of secondary phases. It is explained how the growth conditions (in particular during the annealing step) influence the secondary phase formation and that sufficient S$_2$ and SnS should be supplied to counteract secondary phase segregation and decomposition of CZTS. These insights are particularly important for the optimization of the conditions during the anneal to grow CZTS thin films. Furthermore, the effect of secondary phases on CZTS is discussed. The ternary phase Cu$_3$SnS$_4$ has a detrimental effect on the CZTS material properties. SnS$_x$ on the other hand improves the photoluminescence yield in the CZTS phase. However, it is difficult to conclude whether the presence of SnS$_x$ can possibly lead to an improvement in CZTS device performance.
3. Electronic properties

The electron orbitals that contribute to the bonds in a crystal lattice form continuous bands. Based on the periodicity of the lattice, the properties of this electronic band structure are continuous throughout the whole material. So the crystal structure shapes the electronic band structure of a solid, defining for example its band gap and the density of states within the bands. Both are very important for the absorption of photons and therefore for materials for solar cell applications. Defects in the structure create deviations from the ideal band structure. They cause doping and free carriers in the material, which are important for conductivity. On the other hand, defects also cause potential fluctuations and act as recombination centers, which can have detrimental effects on the solar cell efficiency. This chapter sheds light on the electronic structure of Cu$_2$ZnSnS$_4$ and the nature of common defects in the material as well as their effect on solar cell devices.

3.1 The band gap of CZTS

Cu$_2$ZnSnS$_4$ is a direct band gap material with strong light absorption. Theoretical investigations predict the band gap at 1.5 eV$^{33,68}$. The most common technique to probe the band gap of a material is from absorption spectra (see Box 3.1). Other parameters of a material relevant for photovoltaic devices that can be extracted from the absorption spectra are the absorption coefficient and sub-band gap absorption due to band tails. The absorption coefficient of CZTS is typically above 10$^4$ cm$^{-1}$ which is reasonable for an absorber material for solar cells. The band gap of CZTS has been assigned with energies ranging from 1.45-1.65 eV based on multiple techniques, including absorption$^{69,70}$, spectroscopic ellipsometry$^{71,72}$, quantum efficiency$^{73,13}$ or photoluminescence excitation$^{12}$. For single crystal CZTS quantum efficiency analysis gave a slightly larger band gap energy of 1.64-1.68 eV and electroreflectance spectroscopy gave even larger band gaps of 1.71 eV$^{74}$. Another study reports the band gap for CZTS single crystals at 1.46 eV based on electroreflectance spectroscopy$^{75}$.

The wide spread of reported values for the band gap is unexpected, because the energy gap between valence and conduction band should be characteristic for the material. However, in CZTS several factors were identified, that can modify the observed band gap. One of the more prominent factors is the degree of cation order (see Chapter 4), which has shown to cause band
Box 3.1: Band gap estimation from absorption spectra

When light shines on an object, the light is either reflected, absorbed or transmitted through the object. (The light can also be scattered, however this part is small and can be neglected if the surface is rather smooth.) If the incident light intensity is known, the transmission and reflection of a sample can be measured to determine the absorption of the sample. The absorption of a material describes the ability of the material to transform the energy of incoming light to (mainly) electronic excitations in the material and is dependent on the thickness of the material by the Lambert-Beer law

\[ I(d) = I_0 \cdot \exp(-\alpha(E)d) , \]

where \( I_0 \) is the intensity of the light entering the material, \( I \) is the light intensity after transmitting through distance \( d \) of the material and \( \alpha \) is the absorption coefficient. The absorption coefficient of a material strongly depends on the energy of the incident light \( E \). For direct band gap materials, the absorption coefficient increases above the band gap energy due to the drastic increase of the joint density of states \( JDOS \) according to the relation

\[ \alpha(E) \propto JDOS \propto \frac{1}{E \sqrt{E - E_g}} . \]

Sub-band gap absorption is attributed to band tail absorption and can be differentiated from absorption above the band gap energy by its logarithmic behavior with energy\(^76\).
gap changes of more than 100 meV (see also Figure 4.3 (a)). Another factor that can change the band gap energy is the cation composition. Additionally, secondary phases which are easily formed during CZTS synthesis (see also Section 2.3) can affect the absorption spectra and hamper the band gap extraction.

The large discrepancy of reported values for the band gap in CZTS might also be caused by the relatively large contribution of band tails to sub-band gap absorption which complicates the extraction of the correct band gap. Such band tails are detrimental for the device performance because they enhance recombination and reduce the open circuit voltage $V_{OC}$. Compared with other competing materials for thin film solar cells, the absorption spectrum of CZTS features by far the strongest contribution of band tails.

The origin of band tails in CZTS are potential fluctuations, which are either due to band gap fluctuations or electrostatic potential fluctuations. The difference between both kinds of potential fluctuations is depicted in Figure 3.1. Electrostatic potential fluctuations cause both bands to shift in parallel (together with the vacuum energy) throughout the material and the band gap, i.e. the energy difference between valence and conduction band, remains constant. Electrostatic potential fluctuations are caused by charged point defects, by structural defects or by impurities. In general, potential fluctuations are expected to occur at regions with a high defect density, such as dislocations, grain boundaries and interfaces. If on the other hand band gap fluctuations are present conduction band and valence band fluctuate independently with reference to the vacuum energy throughout the material. As a consequence the energy difference between valence and conduction band is not constant anymore but the band gap varies throughout the material. Band gap fluctuations can be induced by composition or crystalline inhomogeneities, secondary phases or stress in the material.

In any real material a combination of both kinds of fluctuations is expected to occur. However, several studies have identified band gap fluctuations as the dominating cause for band tails in CZTS. Considering Cu-Zn disorder, as discussed in Chapter 4, both types of potential fluctuations are possible consequences. On one hand Cu-Zn disorder causes band gap changes which could lead to band gap fluctuations. On the other hand, clustering of Zn-rich and Cu-rich motifs could create charged domains which could generate electrostatic potential fluctuations.

## 3.2 Defects in CZTS

Defects are features in the crystal where the crystal symmetry is broken, i.e. where the atomic arrangement deviates from the ideal crystal structure. Such defects can be extended defects, such as dislocations, stacking faults, grain boundaries, interfaces or the surface. Defects that only involve one lattice
site are called point defects. Different kinds of point defects are depicted in Figure 3.2. Point defects that cause deviation from the octet rule are easily ionized by binding an electron (acceptor) or releasing an electron (donor). In CZTS the Cu on Zn antisite (CuZn) and the copper vacancy (VCu) have the lowest formation energies and are therefore expected to be the most common defects. Both of these defects are acceptors and therefore generate holes as carriers in the crystal, yielding p-type conductivity for CZTS. Indeed, p-type conductivity has been confirmed in several experimental reports.89,90

Free electrons or holes can interact with ionized defects and by neutralizing them, the free carriers are bound or trapped by the defect. If the ionization energy is small, in the order of the thermal energy $k_B T$, the carrier is easily released again and the effect of the defect is less severe. Defects with small ionization energy are called shallow defects. Analogously, defects with an ionization energy much larger than $k_B T$ are called deep defects. Instead of releasing the bound carrier after ionization, it is more likely that the carrier re-
Photoluminescence is the emission that is released upon radiative recombination of an electron and a hole, which were prior excited by an incoming photon. After excitation, the carriers thermalize to the band edges and possibly defect states within the band gap before recombining. A photoluminescence spectrum therefore contains information about the recombination mechanisms of a material. The energy of the photoluminescence indicates the energy difference of the bands or the energy position of defects within the bands. The photoluminescence yield gives information about the rate of radiative recombination.

Different recombination processes can be identified in photoluminescence spectra: (a) band-to-band recombination, (b) free-to-bound recombination and (c) bound-to-bound recombination, also called donor-acceptor-pair (DAP) recombination (see Figure). They can be differentiated by the energy of the emission, their dependence on the intensity of the incoming light, their temperature behavior or by their transients.

combines with another hole or electron. Therefore, deep defects act as recombination centers and are detrimental to devices. The V_{Cu} in CZTS is regarded as a shallow defect, while Cu_{Zn} has a higher ionization energy and is more likely to act as a recombination center. Recombination has a detrimental effect on the open circuit voltage $V_{OC}$ of solar cells (see also Equation 1.4) and the investigation of recombination processes is therefore of wide scientific interest. A common technique to investigate radiative recombination processes in a material is by photoluminescence spectroscopy (see Box 3.2).

So far only intrinsic defects have been considered. Extrinsic defects are formed if another element is introduced to the crystal, which is not part of the ideal lattice. A typical dopant for CZTS is sodium Na. Na in the CZTS thin film improves the device performance by enhancing the growth and improving the electrical properties. However the exact reason for the improvement is still under debate. One assumption, which has been proposed for the similar material Cu(In,Ga)Se$_2$, is that Na forms antisites on Cu sites Na$_{Cu}$ during the growth but is released later leaving behind the shallow acceptor V$_{Cu}$. Another assumption is that Na locates at the grain boundaries and passivates them. A positive effect has been also observed for other light alkali elements and hydrogen. Another dopant with positive effect on device performance is germanium Ge. A reduction of band tailing and efficiencies of up to 12.3% were achieved with a low open voltage deficit of 548 meV by supplying relatively high doping levels of up to 1% of Ge. Again, the exact mechanisms for the improvement are unclear. Grain boundary passivation, reduction of Sn-related defects and a positive influence on the growth mecha-
nism reducing Sn loss have been hypothesized. The research covered by this thesis mainly concerns intrinsic point defects and defect complexes. Doping with other elements and extrinsic defects will not be elaborated further.

3.3 Defect complexes

Due to the coulomb interaction between two ionized defects, it is favorable to form defect complexes compared to independent point defects. This is illustrated by the following reaction describing the equilibrium between two single defects and a defect complexes

\[ V^-_{\text{Cu}} + Zn^{+}_{\text{Cu}} \rightleftharpoons (V^-_{\text{Cu}} + Zn^{+}_{\text{Cu}}) \]  

In CZTS, defect complexes have much lower formation energies and appear in much larger numbers than independent point defects. Defect complexes do not contribute to the doping level of the material, because the charge of the involved ionized defects is compensated and the defect complexes have an overall neutral charge.

The defect complex \((Cu_{\text{Zn}} + Zn_{\text{Cu}})\) has the lowest formation energy\(^{97,88}\), which explains its abundance and Cu-Zn disorder in CZTS. The Cu-Zn antisite defect complex affects the band gap\(^{77}\) and may be one of the reasons for band gap fluctuations. This defect complex and Cu-Zn disorder is discussed thoroughly in Chapter 4.

The Cu-Zn defect complex and the other defect complexes of opposite antisites, \((Cu_{\text{Sn}} + Sn_{\text{Cu}})\) and \((Sn_{\text{Zn}} + Zn_{\text{Sn}})\), do not cause composition fluctuations. Off-stoichiometric single phase CZTS is therefore connected with the formation of other defect complexes. As a result of the width of the phase stability region, a large amount of defects are expected for off-stoichiometric CZTS and it is reasonable to assume that the majority of these defects arrange in defect complexes. A set of likely defect complexes was established to explain off-stoichiometric CZTS. The proposed defect complexes were based on the observed compositions of single phase \(Cu_2ZnSn(S,Se)_4\) and the point defects identified by neutron diffraction on \(Cu_2ZnSnSe_4\) powders\(^{29,63,98,62}\). The defect complexes are summarized in Table 3.1 and the resulting composition range based on each defect complex is visualized in the composition diagram in Figure 3.3. CZTS can contain a mixture of two neighboring types in order to yield compositions across the whole single phase composition region.

So far, the experimentally verified defect complexes include A-, B-, D-, F-, and G-type\(^{99,100,62,58,101}\). Defect complexes forming in Sn-rich compositions could not be studied by neutron diffraction due to the limitations in powder fabrication to produce Sn-rich CZTS as discussed in Section 2.3. Based on the framework established in Paper III, which was also explained in Section 2.3, particularly Reaction 2.5, defect complexes A, E, H and J will be affected by the SnS and \(S_2\) partial pressures during fabrication and indeed these are the
Figure 3.3. CZTS types against composition. The typical composition region of precursors used for device fabrication is marked in green.

Table 3.1. CZTS types and their intrinsic defect complexes, according to Refs. 29,99, 100,62,58.

<table>
<thead>
<tr>
<th>CZTS-type</th>
<th>defect complex</th>
<th>CZTS-type</th>
<th>defect complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-type</td>
<td>$[\text{VCu} + \text{ZnCu}]$</td>
<td>D-type</td>
<td>$[\text{CuZn} + \text{Cu}]$</td>
</tr>
<tr>
<td>B-type</td>
<td>$[2\text{ZnCu} + \text{ZnSn}]$</td>
<td>C-type</td>
<td>$[2\text{CuZn} + \text{SnZn}]$</td>
</tr>
<tr>
<td>E-type</td>
<td>$[2\text{VCu} + \text{SnZn}]$ or $[2\text{SnCu} + \text{VZn} + \text{VCu}]$</td>
<td>F-type</td>
<td>$[2\text{Cu}_i + \text{ZnSn}]$ or $[\text{CuSn} + \text{Zn}_i + \text{Cu}_i]$</td>
</tr>
<tr>
<td>G-type</td>
<td>$[\text{ZnSn} + \text{Zn}_i]$</td>
<td>H-type</td>
<td>$[\text{SnZn} + \text{VZn}]$</td>
</tr>
<tr>
<td>I-type</td>
<td>$[\text{CuSn} + 3\text{Cu}_i]$</td>
<td>J-type</td>
<td>$[\text{SnCu} + 3\text{VCu}]$</td>
</tr>
</tbody>
</table>
CZTS types that have proven to be challenging to achieve in powder CZTS samples. It should be noted, that the affected defect complexes are also the ones that contain vacancies.

The charge compensation in defect complexes implies that they are not as harmful recombination centers as independent, charged defects. However, since defect complexes disrupt the crystal periodicity they can still act as scattering centers and reduce the life time of free carriers. Furthermore, first principle DFT calculations predict that defect complexes cause changes in the band gap which lead to band gap fluctuations\textsuperscript{97,30}. Especially defect complexes involving the defects Sn\textsubscript{Zn} and Sn\textsubscript{Cu} are expected to cause band gap fluctuations of up to 0.4 eV\textsuperscript{30}. In contrast, A- and B-type defect complexes are more benign to the material properties and should not have a major effect on the device performance.

Due to the dependence of the occurrence of defects on the CZTS composition, the composition has a major impact on the solar cell performance. Based on theoretical predictions, Cu-rich CZTS is expected to yield a very high density of Cu\textsubscript{Zn} antisites, causing high doping levels and detrimental recombination centers\textsuperscript{88}. The deep defect Sn\textsubscript{Zn} in Sn-rich CZTS will have severe effects on the non-radiative recombination rate, considering that not all defects will be paired as (more benign) defect complexes. On the other hand, the shallow acceptor V\textsubscript{Cu} should have a positive effect on the solar cell performance in Cu-poor CZTS\textsuperscript{88}. The A-type defect complex is expected to have the most benign effects on the solar cell performance\textsuperscript{97}. The theoretical predictions explain why CZTS solar cells with highest efficiencies are fabricated with CZTS with Cu-poor and Zn-rich composition\textsuperscript{13,19,14}.

The experimental investigation regarding the nature of defects in CZTS is challenging based on the high defect densities. The investigation of composition-spread samples can offer a broader picture of the impact of composition on the effects of intrinsic defects. Devices fabricated from composition-spread CZTS samples yielded best device performance in the region of A-type and B-type CZTS, however with different maxima with regard to composition for the current $J_{SC}$ and the voltage $V_{OC}$\textsuperscript{102,103,104}.

In Paper V the effect of CZTS composition on the photoluminescence intensity is studied using composition-spread CZTS thin films. Figure 3.4 shows the PL yield against composition for two composition-spread CZTS thin films annealed under different conditions. The photoluminescence intensity does not vary significantly throughout the single phase region of both samples which implies that the main path for non-radiative recombination is not caused by composition dependent defect complexes. Instead, the overall low photoluminescence yield throughout the single phase region indicates the presence of a detrimental defect or defect complex unaffected by the composition. Different explanations are possible, such as a charged defect with low formation energy throughout the single phase region, or S-related defects such as $V_{S}$, which are predicted to act as a detrimental recombination sites from theoreti-
Photoluminescence yield of composition-spread CZTS thin films annealed (a) under typical anneal conditions and (b) in higher S and SnS partial pressures. Secondary phase boundaries are marked with white dotted and dashed lines. Adapted from Paper V.

Another possible explanation could be recombination due to extended defects, such as dislocations, stacking faults or grain boundaries. Such defects appear in much higher number in CZTS with stoichiometric composition compared to Sn-rich CZTS, as discussed in the previous chapter (see Figure 2.4).

A low photoluminescence yield implies that non-radiative recombination is dominating in a material. Because recombination has severe effects on the open circuit voltage $V_{OC}$ (as explained by Equation 1.4), the photoluminescence yield is also an indicator for the potential of an absorber material to reach a satisfactory open circuit voltage. Hence, the low photoluminescence yield throughout the whole CZTS single phase region is worrisome, because it indicates that the $V_{OC}$ will be limited for CZTS solar cells independent of the the cation composition.

This chapter summarizes the electronic properties of CZTS including the band structure and the effect of different types of defects. Band gap fluctuations and electrostatic potential fluctuations are exploited as origin for the severe level of band tailing observed for CZTS and the effects of extended defects, point defects and defect complexes are discussed. Based on findings from literature, the defects SnZn and SnCu act as detrimental recombination centers and therefore Sn-rich compositions should be avoided for CZTS devices. Our own results from photoluminescence investigations on composition-spread CZTS films do not reflect the expected dependence on the composition. Instead, it appears that a composition-independent defect is limiting the photoluminescence yield in CZTS throughout the whole single phase region.
4. Cation disorder in CZTS

The concept of order and disorder in solids is a wide field of research on its own. It stretches from short-range order in amorphous materials to long-range ordered crystals which are categorized by their lattice symmetries and is applied to understand the solid-liquid phase transition. This chapter summarizes the current understanding of cation disorder in Cu₂ZnSnS₄ where the long-range order is broken. Different theories are introduced describing long-range order in solids and their concepts are used to interpret cation disorder in Cu₂ZnSnS₄ and its implications.

4.1 Disorder in CZTS

The CZTS crystal is made up of copper (Cu), zinc (Zn), tin (Sn) and sulfur (S) atoms (see also Fig. 2.1). Possible candidates for antisite pair formation, which could lead to disorder in the crystal, are the cations Cu, Zn and Sn. In the literature the term “disorder” can also be found applied to the occupation of the anion site in Cu₂ZnSn(S,Se)₄ (CZTSSe) containing sulfur and selenium. However, this thesis is concerned with the pure sulfur compound and disorder involving the anion site is not considered.

The crystal radii and charge states of the cations of CZTS are listed in Table 4.1. Zn and Cu ions have the same size in the CZTS crystal which should facilitate antisite formation between both atom kinds, whereas the Sn cation is somewhat smaller and exchange of Sn with either Zn or Cu is less likely. Another indicator is the charge of the cations. The more similar the cations are in their charge, the more likely it is for them to form an antisite defect pair. This is reflected by the calculated formation energies which are listed for all combinations of the three cations in Table 4.2. As predicted from the cation radii and charge, the formation energy of the antisite pair involving Cu and Zn is the lowest and therefore the most likely antisite pair formed in CZTS.

The formation energies for all three antisite pairs are positive and the defect pair is formed at the cost of energy. The crystal without defect pairs should be the energetically favorable state for the system. However the free energy \( F \), which indicates if a system is energetically favorable, is defined as

\[
F = U - TS .
\]  
(4.1)

The formation energy is contained in the internal energy \( U \). The second term in Equation 4.1 is a product of the temperature \( T \) and the entropy \( S \) which is
Table 4.1. Effective cation radii for crystals of coordination number 4 (tetrahedral structures) and the respective charge states of the cation, according to Ref. 108.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Charge</th>
<th>Cation radius (in Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>+1</td>
<td>0.74</td>
</tr>
<tr>
<td>Zn</td>
<td>+2</td>
<td>0.74</td>
</tr>
<tr>
<td>Mn</td>
<td>+2</td>
<td>0.8</td>
</tr>
<tr>
<td>Sn</td>
<td>+4</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Table 4.2. Formation energies (in eV) for antisite pairs from Ref. 88.

<table>
<thead>
<tr>
<th>Defect cluster</th>
<th>Cu\textsubscript{Zn} + Zn\textsuperscript{2−} \textsubscript{Cu}</th>
<th>Cu\textsuperscript{3+} + Sn\textsuperscript{2+} \textsubscript{Cu}</th>
<th>Zn\textsuperscript{2−} + Sn\textsuperscript{2+} \textsubscript{Zn}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation energy (eV)</td>
<td>0.21</td>
<td>1.99</td>
<td>0.86</td>
</tr>
</tbody>
</table>

defined as

\[ S = k_B \ln \Omega . \] (4.2)

The entropy \( S \) depends on the Boltzmann constant \( k_B \) and on the number of possible states or configurations of a system \( \Omega \). If \( \Omega \) increases, the entropy of a system increases. Based on the negative sign in Equation 4.1 higher entropy is favorable for a system (note that this applies at finite temperature, i.e. \( T > 0 \)). In the case of CZTS, the perfect crystal without any defects has only one possible configuration and the entropy is zero. If a Cu-Zn antisite pair is introduced, four different configurations are possible considering only the Cu-Zn planes of one unit cell. Therefore, the entropy of the system is increased by introducing a Cu-Zn disorder pair, which results in a lower free energy \( F \) and an energetically more favorable state of the system.

Cu-Zn disorder was experimentally verified by neutron diffraction on CZTS powders\textsuperscript{35}. It was mainly observed within the Cu-Zn planes (Rietvelt positions 2c and 2d), while the 2a Rietvelt position in the Cu-Sn planes appeared unaffected and only occupied by Cu. Later studies show contradicting results as to whether the Cu atoms on 2a positions are involved in the Cu-Zn disorder transition\textsuperscript{109,100}. Theoretical studies also claim that Cu-Zn disorder should not be restricted to the 2c and 2d positions of Cu-Zn planes, but also involve 2a Cu sites in the Cu-Sn planes. Although, there may be a preference for Zn to form antisites within the Cu-Zn planes\textsuperscript{97,110}. To this date it is not certain whether the 2a sites are involved in the Cu-Zn disorder and if so under which conditions. It is plausible that composition and morphology of CZTS play a role.

The direct measurement and quantification of Cu-Zn disorder in CZTS is difficult, especially for thin film samples. Common methods to quantify Cu-Zn disorder are neutron diffraction\textsuperscript{63,28}, resonant X-ray diffraction\textsuperscript{111}, synchrotron radiation X-ray diffraction\textsuperscript{112} and anomalous diffraction\textsuperscript{113}. These methods allow the analysis of the occupation of certain crystallographic sites including the fraction of disordered and ordered Cu and Zn atoms. However, they require larger samples sizes, typically in the form of powder sam-
ples and are unsuited to study thin film samples. One method to observe cation disorder in thin film CZTS is atomic resolution transmission electron microscopy\textsuperscript{114,115}. But this method is impracticable to study disorder on a macroscopic scale and for a large sample number. Instead, Cu-Zn disorder in CZTS thin films is investigated indirectly by studying effects of disorder on optical and structural properties of the material. The effect of Cu-Zn disorder on the material properties of CZTS and possible methods to study disorder in CZTS thin films will be further explained in Section 4.3.

4.2 The concept of disorder in solids – putting a number on disorder

Bragg and Williams published a series of papers about disorder in solids during the 1930’s to explain experimental observations of atomic re-arrangement in crystalline Au-Cu and Fe-Al metal alloys for temperature treatments well below their melting temperatures\textsuperscript{116}. The order-disorder transition (ODT) in a solid differs from other phase transitions in being a continuous change of the atom arrangement rather than an abrupt reorientation as is observed for a transition between two crystal structures. This is why this transition is classified as a second order phase transition.

To demonstrate the concept of disorder in solids one can define a binary compound with a ground state structure where the lattice sites $\alpha$ are occupied by the atom type $A$ and lattice sites $\beta$ are occupied by atom type $B$. If the compound experiences disorder, some lattice sites $\alpha$ may be occupied by atom type $B$ and some lattice sites $\beta$ by atom type $A$. Bragg and Williams introduce the degree of order $S$ for a material\textsuperscript{116} based on $P_A^\alpha$, the current probability of the site $\alpha$ to be occupied by atom type $A$, and $r$, the probability of the site $\alpha$ to be occupied by $A$ at complete disorder,

$$S = \frac{P_A^\alpha - r}{1 - r}.$$  (4.3)

Note that the degree of order $S$ is not identical to the entropy $S$ of the system which is defined in Equation 4.2. In Equation 4.3 the degree of order is defined in such a way that $S = 0$ if $A$ and $B$ are randomly distributed among $\alpha$ and $\beta$ sites and $S = 1$ if all $\alpha$ sites are occupied by $A$ (and all $\beta$ sites by $B$).

For a theoretical interpretation, Cu-Zn disorder in CZTS is usually reduced to disorder in the Cu-Zn planes for simplification. This way, the kesterite structure can be reduced to a two-dimensional crystal of Cu and Zn atoms and the degree of order $S$ from Equation 4.3 can be rewritten to

$$S = 2P_{Cu}^C - 1 ,$$  (4.4)
with $P^C_{Cu}$ the probability to find a Cu atom on a Cu site (on the Cu-Zn planes). If the crystal is fully ordered, $P^C_{Cu} = 1$ and $S = 1$. If the crystal is completely disordered, $P^C_{Cu}$ reduces to 0.5 and $S$ becomes zero.

The formation of disorder in a crystal is driven by the entropy, as has been explained in the previous section. According to Equation 4.1 the effect of entropy on the free energy depends on the temperature. Therefore, also the equilibrium state of the degree of order $S_e$ depends on the temperature $T$ of the system. Complete order with $S_e = 1$ is achieved only at $T = 0$ K because then the term with the entropy $S$ in Equation 4.1 becomes zero and the most favorable state of the system is the ordered crystal with the lowest formation energy.

High temperature implies that the entropy has a stronger effect on the free energy and disorder becomes more favorable. At the same time thermal agitation increases, which facilitates the formation of antisite pairs when atoms exchange sites with their neighboring atoms. As the temperature increases, the number of antisite pairs, i.e. the degree of disorder, increases and the system will approach an equilibrium state with a degree of order $1 > S_e > 0$. At some temperature the lattice sites $\alpha$ and $\beta$ are randomly occupied by $A$ and $B$, i.e. $S_e = 0$. This temperature is called the critical temperature $T_c$. For any temperature above $T_c$ the degree of order will be zero. The dependence of the degree of order $S_e$ on the temperature for a system in equilibrium is depicted in Figure 4.1.

Scragg et al.\textsuperscript{117} investigated the degree of order of CZTS after thermal treatments at several temperatures and determined the equilibrium curve for CZTS (see Fig. 4.1). They found the critical temperature of the ODT in CZTS at 265 °C. In the selenide compound Cu$_2$ZnSnSe$_4$ (CZTSe) the critical temperature was found somewhat lower at 200 °C.\textsuperscript{77}

Both critical temperatures are well below typical annealing temperatures that CZTS and CZTSe samples are exposed to during fabrication (see Sec-
The kesterites should be completely disordered in the Cu and Zn lattice sites during the high temperature anneal. Once the annealing time is up, the samples are often cooled down quickly and the Cu and Zn atoms do not have enough time to undergo ordering transitions. Instead, the disordered state of the system is frozen and at low temperatures the ordering rate is negligible. Therefore, it can be assumed that the samples are highly disordered without further ordering treatments.

The rate at which a system approaches its equilibrium state $S_e(T)$ depends on certain system parameters and on the temperature. For higher temperatures the rate will be higher, for lower temperatures it can require a relatively long time to reach the equilibrium state. This way it is possible to “freeze” a crystal in a state of low order by fast cooling to lower temperatures where the ordering kinetics are very slow. This implies, that the system is not in equilibrium anymore (i.e. $S \neq S_e$).

The theory of Vineyard\textsuperscript{118} is more suited to study the degree of order for a system that is not in equilibrium. Vineyard derives a relation for the ordering kinetics $dS/dt$ by introducing the rate of ordering $K_O$ and the rate of disordering $K_D$ for a system. If the system is at equilibrium $K_O = K_D$, and $K_O > K_D$ ($K_O < K_D$) if the degree of order is lower (higher) than $S_e(T)$. For a stoichiometric compound ($N_\alpha = N_A$ and $N_\beta = N_B$) the relation for the ordering kinetics is given as

$$\frac{dS}{dt} = \frac{1}{f_B} \left[ K_O f_B f_A (1 - S)^2 - K_D (f_A + f_B S) (f_B + f_A S) \right], \quad (4.5)$$

where $f_A$ and $f_B$ are the fractions of atom kind A and B.

The theory of Vineyard was applied to the disorder in the Cu-Zn planes of Cu$_2$ZnSnSe$_4$ by Rey et al.\textsuperscript{77} and Equation 4.5 can be rewritten to

$$\frac{dS}{dt} = \frac{1}{2} \left[ K_O (1 - S)^2 - K_D (1 + S)^2 \right]. \quad (4.6)$$

Assuming a direct exchange mechanism, the rate constants $K_O$ and $K_D$ for two-dimensional Cu-Zn planes can be expressed as

$$\frac{K_O}{K_D} = 4f \exp \left( \frac{-U}{k_B T} \right) \exp \left( \pm \frac{3vS}{k_B T} \right), \quad (4.7)$$

with $v$ the nearest neighbor interaction energy, $f$ the frequency of the lattice vibration of the atomic interchange and $U$ the activation energy associated with the atomic interchange.

The nearest neighbor interaction energy $v$ is directly proportional to the critical temperature with the relation

$$\frac{v}{k_B} = \frac{2}{3} T_c, \quad (4.8)$$
Table 4.3. Kinetic parameters of the order-disorder transition in B-type CZTS from Paper I.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f$</td>
<td>$9 \times 10^{12}$ Hz</td>
<td>$18500$ K</td>
</tr>
<tr>
<td>$U/v_B$</td>
<td>$358$ K</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.2. Optimized cooling profile with maximum achievable degree of order through thermal treatments. Taken from Paper I.

which was derived in Paper II. In Paper I, the remaining two kinetic parameters $f$ and $U$ were determined for the ODT in B-type CZTS as listed in Table 4.3. Once the parameters $f$, $v$ and $U$ are known, the degree of order $S$ can be estimated for an arbitrary temperature profile $T(t)$ by numerical integration of Equation 4.6 with reasonably small time intervals $dt$.

Furthermore, in Paper I an optimized cooling profile is derived from Equation 4.6 which gives the highest possible degree of order by thermal treatments within a certain time. The optimized cooling profile together with the evolution of the degree of order $S$ are illustrated in Figure 4.2. On one hand, this figure can be regarded as a guide to optimize thermal treatments to achieve a high degree of cation order in CZTS. On the other hand, it reveals that thermal treatments alone cannot effectively reduce Cu-Zn disorder based on the slow ordering kinetics at lower temperatures. Though, it should be noted that a higher degree of cation order $S > 0.8$ upon thermal treatments has been observed in single crystal CZTS\textsuperscript{98,74}, which indicates that the ordering kinetics differ for thin film samples and single crystals.

Applying theories of disorder in solids to Cu-Zn disorder in CZTS naturally comes with limitations and weaknesses. The theories are limited to compounds with stoichiometric composition, and an initial state of order $S$ which
4.3 Cu-Zn disorder in kesterite CZTS

The effect of Cu-Zn disorder on the CZTS material properties can be studied by exposing the material to different thermal treatments below the critical temperature which should change the degree of order of the lattice. It is important to distinguish between permanent structural changes that could arise upon thermal treatments and changes related to the order-disorder transition, which should be completely reversible upon further thermal treatments. This way it is possible to correlate the observed changes upon thermal treatments with changes in the degree of Cu-Zn order and the findings of such studies are summarized in this section. For the experimental studies of cation disorder of this thesis, the low temperature treatments to promote cation order were performed in the same tube furnace which was also used for crystallization anneals of the precursors as described in Section 2.2. This setup allowed the treatments to take place in a constant argon atmosphere and it allowed exact temperature control and monitoring of the sample temperature during the whole treatment.

As was discussed in Section 4.1, methods for direct quantification of the degree of disorder in CZTS are not suited for the investigation of thin films samples. Therefore, other methods were developed to estimate the degree of disorder in CZTS thin films by studying the effects of Cu-Zn disorder on different CZTS properties.

The degree of Cu-Zn order has a drastic effect on the band gap of CZTS, which is narrowed substantially when decreasing the degree of Cu-Zn order. Valentini et al.\(^{119}\) observe a band gap change of up to 150 meV for one sample upon thermal treatments. Theoretical predictions based on DFT calculations predict changes of the band gap of 130 meV\(^{120}\) and 200 meV\(^{117}\) based on Cu-Zn disorder which are in the range of experimental observations. The narrowing of the band gap is explained by a larger density of the defect pair (Cu\(_{Zn}\)+Zn\(_{Cu}\)) which creates defect levels within the band gap and by that contributes to an overall reduction of the band gap. The effect of band gap changes upon ordering can be observed by different techniques, such as spec-
Figure 4.3. a) Band gap widening after thermal ordering treatments observed in quantum efficiency spectra. b) Changes in the Raman spectra of CZTS thin films that can be correlated with different degrees of order. Taken from Paper I.

trophotometry\textsuperscript{77}, photoluminescence spectra\textsuperscript{121} or quantum efficiency (see Figure 4.3 (a)). Consequently, Rey et al. utilized the effect of Cu-Zn disorder on the band gap shift of CZTSe thin films to estimate the degree of order \( S \)\textsuperscript{77} and proposed a method to analyze the degree of order for thin films.

Analogously, the effects of Cu-Zn disorder on the Raman spectra of CZTS have been correlated with the degree of order \( S \)\textsuperscript{31} to yield a method to analyze Cu-Zn disorder in CZTS thin films. The Raman spectrum of CZTS (in backscattering configuration) consists of the intense A mode at 338 cm\(^{-1}\) and another A mode at 289 cm\(^{-1}\). Under resonant excitation, B and E modes between 250 cm\(^{-1}\) and 380 cm\(^{-1}\) become clearly visible as well. Two major effects can be detected with reducing cation order: widening of the full width half maximum (FWHM) of the main peak at 338 cm\(^{-1}\) and a change in the peak height ratios involving the peaks at 289 cm\(^{-1}\), 305 cm\(^{-1}\), 367 cm\(^{-1}\), and 377 cm\(^{-1}\) (see Figure 4.3 (b)).

The widening of the FWHM for more disordered CZTS seems plausible based on the assumption that disorder in the Cu-Zn planes compromises the crystallinity of the CZTS material as a whole. With reduced crystal quality, the phonons in the crystal will be confined to a smaller volume. According to the phonon confinement model, this causes the Raman modes to widen and shift slightly to smaller wavenumbers\textsuperscript{122}, as is observed in the Raman spectra in Figure 4.3 (b) for CZTS with less cation order.

Paris et al.\textsuperscript{67} focus on the changes of the relative peak heights in the Raman spectrum after thermal ordering treatments and define the two parameters \( Q \) and \( Q' \) based on the peak heights of the Raman modes

\[
Q = \frac{H_{289}}{H_{305}} \quad \text{and} \quad Q' = \frac{H_{338}}{H_{367} + H_{377}}. \tag{4.9}
\]

In Paper I it is proposed that the relative peak heights defining the parameter \( Q \) change because of a change of the crystal symmetry from ordered kesterite
I\textsuperscript{4} to disordered kesterite I\textsuperscript{4}2m, which is the same symmetry group as the stannite crystal. Crystals of the kesterite symmetry group I\textsuperscript{4} feature three A-modes in their Raman spectra. In the symmetry group I\textsuperscript{4}2m, two of these A-modes are degenerate and instead only two A-modes are distinguishable in the Raman spectrum. Therefore, it is expected that one of the A-modes reduces in intensity as CZTS becomes more disorder and resembles a crystal with I\textsuperscript{4}2m symmetry. This could explain the reduction in intensity of the mode at 289 cm\textsuperscript{-1} which has been identified as one of the A-modes for CZTS. This would imply, that a completely disordered CZTS crystal with I\textsuperscript{4}2m symmetry should not feature any intensity for the Raman mode at 289 cm\textsuperscript{-1}, resulting in \( Q = 0 \).

In Paper I the \( Q \) parameter was used to quantify the degree of order for a series of B-type CZTS thin films that had been exposed to different thermal ordering treatments. The temperature profiles of the ordering treatments were additionally evaluated with the theory by Vineyard (Equations 4.6 and 4.7) and a linear relation \( S(Q) \) was derived

\[
S = (0.18 \pm 0.02)Q. \tag{4.10}
\]

It should be noted, that this linear relation passes through zero, which is expected if the changes in \( Q \) originate from a symmetry change of the CZTS crystal due to disorder as explained in the previous paragraph.

In Paper II the correlation between the parameters \( Q \) and \( Q' \) and disorder in CZTS was verified for the full composition region of CZTS by investigation of composition-spread thin films. It was demonstrated that both parameters correlate with the FWHM of the main CZTS Raman peak at 338 cm\textsuperscript{-1} which led to the conclusion that both parameters reflect the state of order of the CZTS material. However, the \( Q \) parameter attained very different values for some composition regions (this is further discussed in Section 5.1) indicating that the relation \( S(Q) \) given in Equation 4.10 only applies to B-type CZTS.

Despite the direct effects of Cu-Zn disorder observed on the band gap and the vibration modes of CZTS, the effect on solar cell devices is still debated. Based on the experimentally observed and calculated effects on the band gap one would predict that an increased degree of order implies less band gap fluctuations which should reduce the open circuit deficit in CZTS based solar cells. Instead, it has not been possible to reduce the open circuit voltage deficit by thermal ordering treatments\textsuperscript{23,123,124,25}. The open circuit voltage was improved, but the band gap increases by the same amount and the deficit of the open circuit voltage remained at the same value. Even though the open circuit voltage deficit could not be reduced, thermal ordering treatments enhanced several material properties in CZTS, such as reduction of free carriers from 10\textsuperscript{18} cm\textsuperscript{-1} to 10\textsuperscript{16} cm\textsuperscript{-1} and higher mobilities\textsuperscript{125}, and higher luminescence intensity implying a reduction in non-radiative recombination\textsuperscript{124}. Furthermore, a positive effect on the fill factor has been observed which led to an overall improvement of device efficiencies\textsuperscript{25,123}. A possible explanation why order-
ing treatments fail to improve the open circuit deficit is discussed in Paper I. It is argued that thermal treatments do not achieve the necessary degree of order in thin film CZTS to reduce the band tailing to a degree where it is not detrimental to the open circuit voltage in solar cells.
5. Defect Engineering in CZTS

Defect engineering aims to control the defects in a material in order to tune the materials fundamental properties, like the band gap and absorption, or (electrical) conduction and recombination processes\textsuperscript{126,127}. In Cu\textsubscript{2}ZnSnS\textsubscript{4} in particular, defect engineering aims to reduce or to passivate Cu-Zn disorder and detrimental point defects like Sn\textsubscript{Zn} and to enhance the hole doping by V\textsubscript{Cu} instead of Cu\textsubscript{Zn}. This has led to Cu-poor and Zn-rich compositions as the preferred compositions for Cu\textsubscript{2}ZnSnS\textsubscript{4} devices. In Papers I – V different strategies for defect engineering are exploited with the aim to control and reduce the Cu-Zn disorder and subsequent band gap fluctuations. This chapter discusses these strategies and puts them into the context of strategies discussed in literature.

5.1 Reducing Cu-Zn disorder in CZTS

The most common way to control Cu-Zn disorder, i.e. the density of (Cu\textsubscript{Zn}+Zn\textsubscript{Cu}) defect pairs, is by temperature treatments as described in Chapter 4. However as discussed in Paper I and illustrated in Figure 4.2, temperature treatments alone do not succeed in reducing Cu-Zn disorder sufficiently in conventional CZTS thin film absorbers, because they would require an extremely long time to produce highly ordered CZTS. Other strategies are needed to reduce the favorability of disorder (i.e. raise T\textsubscript{c}) or to enhance the ordering kinetics and by that boost the effect of temperature treatments.

As derived in Equations 4.6 and 4.7 the kinetics of the ordering process \( \frac{dS}{dt} \) are governed by the frequency of the lattice vibration of the atomic interchange \( f \), the nearest neighbor interaction energy \( v \), and the activation energy associated with the atomic interchange \( U \). In order to change the ordering kinetics, one has to find a way to manipulate one or more of these parameters. The frequency of the lattice vibration \( f \) depends on the mass of the involved atoms in the lattice and their bonds. This frequency is not very sensitive to minor changes to the lattice such as doping and effects on this frequency should be visible in the Raman spectrum. The nearest neighbor interaction \( v \) describes the energy difference of the system before and after the cation exchange and is directly proportional to the critical temperature of the order-disorder transition as was shown in Equation 4.8. \( U \) on the other hand is the activation energy of the cation exchange. Figure 5.1 visualizes the two parameters \( v \) and \( U \). To enhance the ordering kinetics, \( v \) should be increased, to boost the driving force
towards the ordered state of the system, while $U$ should be lowered to enhance the cation exchange process.

In Paper II the effect of the cation composition on the ordering kinetics is investigated on a composition-spread CZTS thin film with a continuous cation gradient. The $Q$ parameter, which is proportional to the degree of Cu-Zn order (see Equations 4.9 and 4.10), was evaluated from resonant Raman spectra and is plotted against the composition in Figure 5.2. The ternary phase Cu$_3$SnS$_4$ leads to a drastic reduction in the $Q$ parameter in Zn-poor compositions outside the single phase region. Otherwise, the composition of Zn within the single phase region does not seem to affect the ordering kinetics. However the $Q$ parameter changed drastically with the Cu/Sn ratio, with lowest values for $Q$ where the Cu/Sn ratio is stoichiometric ($\text{Cu/Sn} = 2$) and higher $Q$ values in Cu-rich and Cu-poor compositions. Further investigations indicated that the critical temperature remains constant for different compositions. Therefore, the change in ordering kinetics can not be due to a change in $v$, but must be caused by a lowered activation energy $U$. The composition regions with higher $Q$ parameter correlate with the composition regions where defect complexes with vacancies or interstitials are expected. Such defects are known to enhance diffusion processes in other materials. Therefore, the observed composition dependence is interpreted as an enhancement of the ordering transition by defect assisted diffusion processes. These results show, that defect engineering using the cation composition to reduce Cu-Zn disorder in CZTS is possible and that higher degrees of order can be achieved in compositions with a high density of interstitials or vacancies.

In Paper III (see also Section 2.3), it was shown that the solubility of defect complexes containing vacancies strongly depends on the processing conditions, in particular on the SnS and S$_2$ partial pressures during the high temperature anneal. By supplying high partial pressures of S$_2$ and SnS, the solubility of defect complexes containing vacancies can be enhanced leading to high densities of vacancies in Sn-rich/Cu-poor CZTS. This should further enhance
the impact of defect assisted diffusion on the ordering kinetics during thermal treatments. Therefore, the partial pressures during the fabrication process should be considered when aiming for a strong effect of vacancy assisted Cu-Zn ordering in Sn-rich compositions.

This is demonstrated in Papers III and V with composition-spread CZTS thin films annealed in different S₂ and SnS partial pressures, see Figure 5.2 (a) and (b). For the sample annealed in higher S₂ and SnS partial pressures (Figure 5.2 (b)), the secondary phase boundary of SnSₓ is shifted to a lower Cu/Sn composition ratio, indicating that the CZTS phase is less likely to decompose for Sn-rich compositions and higher defect densities in CZTS should be attained. Indeed, the $Q$ parameter is strongly enhanced in the Sn-rich composition region indicating a higher density of vacancies. The $Q$ parameter was even further enhanced in Zn-poor composition regions close to the secondary phase boundary of Cu₃SnS₄. This effect has not been explained yet. It could be connected to the presence of Cu₅Zn antisites, either as independent point defects or in defect complexes. The full width half maximum of the main vibration mode in the Raman spectra showed the same trends across the composition-spread samples as the $Q$ parameter, confirming that $Q$ predicts changes in the crystalline quality.

The results presented in Papers III and V are promising that there is still room for improvement in the ordering kinetics through defect engineering by tuning the density of the internal CZTS defect complexes. The results demonstrate that it is important to consider not only the cation composition of the precursor, but also the annealing conditions to reach CZTS with desirable properties.

CZTS based solar cells suffering from band tailing due to the cation disorder could benefit from a higher density of vacancies in Sn-rich compositions, especially with a high density of A-type defect complexes ($V_{Cu} + Zn_{Cu}$). First
principle calculations predict that the reduction of the band gap by the Cu-Zn antisite complex can be counteracted, or passivated, by the A-type defect complex due to its opposite effect on the CZTS band gap. Other studies have reported beneficial effects of Sn-rich composition on CZTS properties, including blue shift of the band gap and reduced sub-band gap absorption and a difference of the ordering kinetics depending on the composition towards A-type CZTS. However, a direct comparison of the reported CZTS compositions and the observed effects on cation disorder and potential fluctuations is difficult. The defect nature and defect densities are likely to differ based on the different employed fabrication conditions and the difficulty to derive the cation composition of the CZTS phase from the integral film composition. Unfortunately, not many studies are available about the effect of Cu-rich compositions. For such compositions the effects should be easier to compare, since the partial pressures during the anneal should not have such a strong impact on the defect nature of the CZTS phase.

5.2 Alloying CZTS with other elements for defect engineering

Another method for defect engineering is by doping or alloying with an impurity element. Both methods have been exploited with several different elements (see the periodic table depicted in Figure 5.3) with the hope to enhance CZTS material properties and to improve the device performance. Doping is typically referred to when adding only small amounts of an impurity ele-
ment with the goal to tune electronic properties, but without changes to the crystal structure of the host material. While the term alloying is referred to when larger amounts (> 1 mol.-%) of another material are introduced to the host material, forming a solid solution. Initially alloying was mainly used to describe metal alloys. In CZTS alloying is often regarded as a partial atom replacement.27

The most common element for alloying with CZTS is selenium (Se). It replaces sulfur in the host lattice and is used to tune the band gap between 1.6 eV with no selenium down to 1.0 eV when replacing all sulfur by selenium. The highest efficiencies for kesterite solar cells were achieved with relatively high selenium contents (Se/(Se+S) > 0.75). This atomic exchange also affects the order-disorder transition by reducing the critical temperature to \( T_{C,\text{CZTSe}} = 200^\circ C \) and by lowering the activation energy \( U \) for the cation exchange compared to CZTS. Despite the lower activation energy, CZTSe suffers from severe Cu-Zn disorder. The highest degree of order \( S \) reported for CZTSe thin films is at around 0.7, which is similar to the amount of disorder expected in CZTS after low temperature ordering treatments (see Paper I).

Other impurity elements were reported to have a positive effect on the Cu-Zn disorder. One of them is silver (Ag), which replaces Cu in the host CZTS lattice. Theoretical calculations predict a higher formation energy of the Zn-Ag antisites and a neutron diffraction study shows that in fact a partial substitution of Cu by Ag suppresses Cu-Zn disorder. Characterizing the optical properties of \((\text{Cu,Ag})_2\text{ZnSnS}_4\) revealed reduced band tailing when the Ag content is increased. The downside of alloying with Ag is that the alloy converts to n-type for higher silver contents which results in poor device performance using the conventional devices stack for kesterite solar cells.

Cadmium (Cd) has also been alloyed with CZTS where it replaces Zn. Calculations predict that already small amounts of Cd can have a positive effect on the Cu-Zn disorder. Relatively high efficiencies were achieved with devices that were produced with \( \text{Cu}_2(\text{Zn,Cd})\text{SnS}_4 \) and one of the observed improvements through Cd alloying was a reduction in band tailing. However, alloying can have several effects on the material properties, e. g. the alloyed element can act as a fluxing agent during the growth (i. e. facilitate the growth and crystallization of CZTS) and suppress secondary phase segregation. Therefore, the observed reduction of band tailing may be caused by other effects of alloying rather than a reduction of Cu-Zn disorder.

The candidates for alloying with CZTS presented here have been chosen as examples for the most promising results in terms of device performance and their effect on Cu-Zn disorder. However, when choosing suitable elements for device fabrication other considerations should not be neglected, such as toxicity (Cd) and scarcity (Se and Ag). Allying CZTS with toxic and scarce materials contradicts the initial attraction that caused the immense interest in CZTS in the first place.
5.3 Exploring cation exchange for materials with preferable properties

An extreme version of alloying is to completely exchange one element in the compound and to form a new compound with the goal to reduce unfavorable defects while sustaining beneficial properties. In the case of CZTS, a cation exchange should ideally reduce cation disorder, but maintain an electronic structure with a direct band gap around 1.5 eV and a high absorption constant. In Paper IV the compound Cu$_2$MnSnS$_4$ (CMTS) is investigated as a potential alternative to CZTS. The Zn cation is replaced by manganese (Mn), which is a non-toxic and abundant transition metal just as Zn. Compared to other abundant transition metals, Mn features the largest difference in cation radius with Cu, which should reduce the probability for cation disorder. Calculations predict the compound to be stable towards decomposition in the stannite ground state structure, which has been confirmed by neutron diffraction. The cation arrangement in stannite CMTS is depicted in Figure 5.4. The compound CMTS has a direct band gap at 1.61 eV with high absorption.

In Paper IV CMTS thin films of different cation compositions were fabricated by adapting the two stage process described in Section 2.2. The thin films were carefully characterized by X-ray diffraction and Raman spectroscopy, which gave evidence for several secondary phases besides the main CMTS phase. Absorption spectra revealed band gap energies in the range 1.42 – 1.59 eV depending on the cation composition and a high absorption coefficient in the order of 10$^4$ cm$^{-1}$. However, low temperature treatments between 160 °C and 300 °C cause reversible changes in the band gap, the Urbach energy and the absorption constant which suggest that CMTS suffers from an order-disorder transition with a critical temperature of 230±10 °C (see Fig-
Figure 5.5. Reversible changes in band gap energy, Urbach tail energy, and absorption constant after thermal treatments at different temperatures. The inferred critical temperature of the order-disorder transition is marked by the grey area. Taken from Paper IV.

Considering the calculated low formation energy of the Cu-Mn antisite pair in CMTS\textsuperscript{120} it is proposed that the order-disorder transition occurs among the Cu and Mn atoms and causes the observed effect of low temperature treatments.

This finding is curious as it demonstrates that cation disorder is probably not restricted to the kesterite lattice, but also exists in the stannite structure. The stannite structure was thought to be immune to cation disorder, because observations based on neutron diffraction found no sign for cation disorder in the stannite Cu\textsubscript{2}FeSnS\textsubscript{4}\textsuperscript{35}. Furthermore, cation disorder in CZTS is often argued to be motivated by the almost equal cation size and the arrangement of the cations in neighboring positions within the same lattice planes. Both features do not apply to stannite CMTS.

The interpretation that stannite CMTS suffers from Cu-Mn disorder in the same way as kesterite CZTS is supported by the calculations of antisite-formation energies in several compounds with the chemical structure Cu\textsubscript{2}XSnS\textsubscript{4}\textsuperscript{120}. Replacing Zn by beryllium (Be), magnesium (Mg), Mn, iron (Fe), or nickel (Ni) does not notably affect the formation energy of the defect.
pair of the \((\text{Cu}_X + X_{\text{Cu}})\) antisite and cation disorder is a likely consequence in all of these compounds, unaffected by their ground state structure.

Nevertheless, different interpretations of the presented results of Paper IV are possible. Previous studies did not consider the effect of disorder during their assignment of the crystal structure of CMTS and it is possible that the stannite phase was assigned by mistake, similar to the discussion of the correct crystal structure of CZTS\textsuperscript{28}. Therefore, two alternative interpretations are given in Paper IV, namely that either kesterite is the actual ground state structure of CMTS, or even though stannite is the ground state structure, the formation energy of disordered kesterite could be more favorable than the stannite configuration. In conclusion, a disorder-free material should (i) not favor disorder in its ground state structure and (ii) lack structural polymorphs that exhibit cation disorder and have similar formation energies as the ground state structure.

The conclusions from Paper IV demonstrate that cation disorder and associated band tailing is not easily avoided by cation replacement with manganese or even other cations. Cation disorder seems to be an inherent characteristic of the kesterite and the stannite structures. More drastic structural changes are necessary to diminish the effect of cation disorder. For example, the compound \(\text{Cu}_2\text{BaSnS}_4\) crystallizes in a trigonal structure which impedes the formation of Cu-Ba antisites. In fact, a less severe effect of band tailing is observed in the photoluminescence and absorption characteristics of the compound\textsuperscript{141}. Nevertheless, solar cells fabricated with a \(\text{Cu}_2\text{BaSnS}_4\) absorber layer only reached efficiencies of 5.2\%\textsuperscript{142}.

Even though plenty of studies explore the possibilities of alloying and cation exchange in CZTS\textsuperscript{26,27}, none succeeded to improve the efficiency of kesterite solar cells. This issue could be related to the difficulty in optimizing critical material properties (such as composition and intrinsic defects), and to finding suitable materials to compliment the material of the absorber layer in the full solar cell stack.
6. Concluding remarks

The previous chapters discuss the findings of the research conducted throughout this PhD in the broader context of the general understanding of CZTS and its material properties. This chapter, however, solely summarizes the results and conclusions that were attained in the scope of this PhD in terms of defect engineering in kesterite Cu₂ZnSnS₄. Section 6.2 is a personal reflection of these results and provides an outlook for future research efforts.

6.1 Summary of the results of this thesis

Defect engineering aims to control the densities of important or detrimental defects in a material. The understanding of the kinetic and thermodynamic effects that govern the formation of these defects can be the key to achieve this goal, or imply limitations of defect engineering in a material. In a defect rich material like Cu₂ZnSnS₄ (CZTS), developing methods for defect engineering presents additional challenges because it becomes difficult to distinguish the effect of individual defects or of specific treatments for defect engineering on the material.

Nevertheless, the research conducted within the scope of this thesis investigated various techniques for defect engineering in CZTS thin films. The ambition of this thesis was to bring a knowledge-led approach to the challenge of defect engineering in CZTS, by connecting observable material properties with the current understanding and perception regarding defect formation and defect kinetics. Raman spectroscopy was the main experimental technique to analyze the change in crystal quality and degree of order upon different methods for defect engineering. Spectrophotomery and photoluminescence gave further insights about the absorption and recombination characteristics of the material, respectively. The investigation of composition-spread samples yielded valuable insights about the interplay of fabrication conditions and phase stability as well as the influence of the cation composition on material properties. Based on the results, the potential of different methods for defect engineering in CZTS to enhance the solar cell conversion efficiency was discussed.

Paper I determined the kinetic parameters for the Cu-Zn order-disorder transition in CZTS. The knowledge of the kinetic parameters allowed to predict an optimized temperature profile for thermal ordering treatments and for the first time the practical limitations for such treatments could be estimated.
The results reveal the slow ordering kinetics and weak driving force for ordering in CZTS with severe implications: thermal treatments alone will not succeed in reducing Cu-Zn disorder in CZTS to an extent where the consequential potential fluctuations are harmless to the open circuit voltage of solar cells, because the treatment would require years. Instead other strategies need to be explored.

**Paper II** represents the first report to demonstrate the influence of the cation composition of CZTS in a wider range on the order-disorder transition. A clear enhancement of the degree of order after thermal treatments was observed for compositions away from the stoichiometric composition ratio of \( \text{Cu/Sn} = 2 \). Further investigations resolved that the composition does not affect the critical temperature of the order-disorder transition, which is proportional to the nearest neighbor interaction energy, i.e. the driving force towards the ordered state. It is concluded that instead the activation energy of the transition is influenced by the Cu/Sn ratio. The enhanced ordering kinetics suggest defect assisted cation exchange mechanisms in Cu-poor and Cu-rich CZTS in the presence of vacancies or interstitials. Therefore, composition tuning is identified as a potential tool for defect engineering in CZTS to reduce cation disorder.

As in Paper II, the experimental approach in **Papers III and V** utilized composition-spread CZTS thin films, i.e. samples with a continuous variation of cation composition across their area. Through both papers, a method has been developed to identify the secondary phase boundaries and the CZTS single phase region by combining composition analysis from energy dispersive X-ray spectroscopy with phase analysis based on multiwavelength Raman spectroscopy and X-ray diffraction. This method yields the unique opportunity to investigate how defect formation is affected by the chemical potentials in CZTS synthesis.

**Paper III** demonstrates how the solubility of vacancies in Cu-poor CZTS can be increased by raising the partial pressures of \( S_2 \) and SnS during the annealing step of the fabrication. The higher density of vacancies results in a further enhancement of the ordering kinetics in Cu-poor CZTS compared to the observations from Paper II. A chemical model describing the solubility of composition dependent defect complexes in CZTS was developed and verified through the observed results. The implications of this model indicate further opportunities for defect engineering in CZTS.

The effect of composition within the single phase region and the influence of secondary phases outside of it were studied in **Paper V**. The positive effect of higher partial pressures of \( S_2 \) and SnS on the density of copper vacancies in Cu-poor CZTS leading to an enhancement in the ordering kinetics, which was already observed in Paper III, was further strengthened. Surprisingly, the photoluminescence intensity followed a different trend with CZTS composition compared to the ordering kinetics. The highest photoluminescence intensity and enhanced morphology were not observed within the single phase region,
but correlated with composition regions where SnS$_x$ secondary phases were present. This indicated that SnS$_x$ secondary phases are necessary for passivating or eliminating detrimental defects. On the other hand, the generally low photoluminescence yield throughout the single phase region was worrisome, as it indicated detrimental defects in CZTS which appear to be unaffected by changes in the chemical potential. Therefore, the results of Paper V imply the potential of defect engineering to enhance the ordering kinetics in CZTS, but also limitations of defect engineering through composition tuning to reduce detrimental defects leading to non-radiative recombination.

**Paper IV** followed a different approach to defect engineering and investigated the potential of cation exchange yielding related compounds to avoid cation disorder. Exchanging one element from the compound should effect the parameters governing the order-disorder transition, i.e. the critical temperature and the activation energy for ordering should be affected. Here, the structural and electronic properties of the compound Cu$_2$MnSnS$_4$ were studied. Even though Cu$_2$MnSnS$_4$ crystallizes in the stannite structure, the compound nevertheless suffers from an order-disorder transition implying that cation disorder is not restricted to kesterite Cu$_2$ZnSnS$_4$. The existence of cation disorder in Cu$_2$MnSnS$_4$ points towards a general problem extending to a variety of compounds containing atom species with similar radii.

### 6.2 Outlook

To my understanding after investigating the CZTS material for a little more than five years, CZTS solar cell conversion efficiencies are currently limited by not one but several deficiencies in the bulk CZTS material: (1) deep defects leading to recombination, e.g. Sn$_{\text{Cu}}$ or Sn$_{\text{Zn}}$, (2) Cu-Zn disorder and (3) morphological problems related to decomposition of CZTS into secondary phases. CZTS (as well as CZTSe) stands out among other solar cell absorber materials as very defect rich and with serious band tailing. Several candidates are discussed to cause these detrimental band tails. Deep defects, such as Sn$_{\text{Zn}}$, or Cu-Zn disorder are the main suspects.

The effect of Cu-Zn disorder on CZTS devices remains unknown. Several studies reported that ordering treatments failed to reduce the open circuit voltage deficit$^{25,123}$, however there is no possible way to be sure as long as we fail to produce highly ordered CZTS thin films. Personally, I am still convinced that Cu-Zn disorder is detrimental to the solar cell performance and (at least) one of the reasons for the observed band tailing. The dramatic change of the band gap with ordering treatments makes it difficult to believe that Cu-Zn disorder could be benign to the electrical properties of CZTS. This being said, the results from Paper I about the limitations of thermal treatments to increase the degree of order should be an eye opener that we either have to learn to live
with Cu-Zn disorder in CZTS and find ways to passivate its effects, or come up with new creative solutions to reduce Cu-Zn disorder.

Some ideas to tackle Cu-Zn disorder are presented and discussed in this thesis: The results from investigations on composition-spread samples suggest that further composition tuning together with novel annealing conditions implementing high S\textsubscript{2} and SnS partial pressures can lead to an immense increase in the degree of order after thermal treatments. The characterization techniques were limited to a qualitative comparison of the degree of order. It would be interesting to investigate the actual level of Cu-Zn order achieved by tuned fabrication conditions.

As intriguing it may be to eliminate Cu-Zn disorder in CZTS, Paper V suggests that other defects limit the photoluminescence yield and drive recombination especially in the single phase region. Instead the limitation seems lifted only in the presence of SnS\textsubscript{x} secondary phases.

The photoluminescence yield of composition-spread samples in Paper V suggests a wide composition region that should be preferable in terms of recombination rates, i.e. compositions where SnS\textsubscript{x} secondary phases form, in the range of A- to E-type CZTS. However, CZTS absorbers of high efficiency solar cells typically exhibit a narrow composition region in the (A+B)-type composition range\textsuperscript{103,104,102,13}. This discrepancy raises uncomfortable questions: Is the high PL-yield for even J- and E-type CZTS only an artifact of composition-spread CZTS? Or is the device stack not optimized for compositions other than B- and A-type CZTS and therefore yields worse efficiency outside this composition region? The positive effects of SnS\textsubscript{x} secondary phases on the material properties poses further questions: Can we achieve highly efficient CZTS solar cells (past 12.6\%), if secondary phases are a necessity for enhanced crystallinity and reduced non-radiative recombination? And what role do SnS\textsubscript{x} secondary phases play in the absorber exactly? Why is the photoluminescence enhanced in the region where the deep Sn-related defects are expected? Last but not least, there is no evidence so far if the high photoluminescence yield and high degree of Cu-Zn order in Sn-rich regions of the composition-spread samples correlate with an improvement in the band tailing.

The research on CZTS is at a turning point as the trend in the record efficiencies stagnates. Turning to new materials is tempting, but our results from Paper IV show that the effect of disorder is most likely not eliminated as long as the cations chosen are similar in their sizes and the compound crystallizes in structures similar to kesterite or stannite.

In the end, my research could not deliver the one solution for an earth-abundant, non-toxic solar cell absorber material. However, I hope that my conclusions can inspire and present new pathways to improve the crystalline quality of thin film solar cell absorbers.
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