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Germanium Incorporation in $\text{Cu}_2\text{ZnSnS}_4$ and Formation of a Sn–Ge Gradient

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Alloying of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) with Ge can potentially promote grain growth and suppress the formation of Sn-related defects. Herein, a two-step fabrication route based on compound co-sputtering and sulfurization at a high temperature is used to prepare Ge-incorporated CZTS ($\text{Cu}_2\text{ZnGe}_x\text{Sn}_{1-x}\text{S}_4$ [CZGTS]). For $\text{Cu}_2\text{ZnGeS}_4$ (CZGS), films deposited using elemental Ge and binary GeS targets are compared. The recrystallization is shown to be promoted for the absorbers deposited using Ge target, possibly due to lower sulfur content in the precursor suppressing the formation of wurtzite-like phases during sputtering. The grain growth and crystallinity in CZGTS are slightly improved for $x=0.2$ but not for higher concentration of the incorporated Ge. Owing to the composition-dependent electronic properties, compositionally graded CZGTS films may be beneficial for reducing recombination towards the back contact. Hence, herein, the successful formation of a steep concentration gradient with Ge and Sn is demonstrated by the deposition of a CZGS/CZTS precursor stack followed by sulfurization with varying time periods.

1. Introduction

The use of earth abundant materials is preferred for terawatt scale energy production and deployment of photovoltaics to cut down carbon emissions in the future.^[1] Non-toxic $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) appears as an attractive material due to suitable optical properties, but the overall efficiency needs to be increased to the level of commercially available solar cells. $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se}_2)$ (CIGS) solar cells have improved steadily up to the current record efficiency of 23.3%.^[2] Some of the important

contributing factors to the success of CIGS solar cells are the possibility of bandgap profiling with In/Ga or S/Se compositional gradients^[3–5] and low density of detrimental bulk defects.^[6–8] CZTSSe is still limited to a reported efficiency of 12.6%^[9] even though several groups have recently reached 11–12% efficiency using different fabrication routes.^[9–14] In this work, alloying of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) with Ge and the formation of a bandgap gradient are studied as potential routes for increased efficiency. Ge is not as abundant as the other elements in CZTS, but is non-toxic and mainly used here as a tool to understand efficiency limitations in CZTS.

CZTS contains different types of bulk defects, both intrinsic and extrinsic, as well as binary or ternary secondary phases due to the non-stoichiometric composition ($\text{Cu}/(\text{Zn} + \text{Sn}) = 0.8$ and $\text{Zn}/\text{Sn} = 1.2$)

optimized for efficient solar cells.^[15] Most defects naturally present in CZTS, however, are harmless for photovoltaics due to their shallow nature.^[16] In contrast, deep Sn-related defects were suggested to be responsible for electron trapping in CZTS, whereas this defect was shown to be less detrimental in $\text{Cu}_2\text{ZnSnSe}_4$ CZTSe.^[17] One of the suggested reasons for such a deep defect character of Sn_{Zn} is $\text{Sn}^{+4}/\text{Sn}^{+2}$ multivalency. In this regard, it was hypothesized that the formation of this deep defect can be suppressed by replacing multivalent Sn with isovalent Ge. Furthermore, first-principles studies indicate that Ge alloying can alter the stability of competing phases in $\text{Cu}_2\text{ZnGe}_x\text{Sn}_{1-x}\text{S}_4$ (CZGTS).^[15] Thus, CZGTS was reported to crystallize in kesterite (KS)^[18] or stannite (SN)^[19] phases (tetragonal structure), which are difficult to distinguish using conventional experimental tools, such as X-ray diffraction (XRD), due to the peak overlap. Stabilization of high-energy wurtzite (orthorhombic) phases was also demonstrated in $\text{Cu}_2\text{ZnGeS}_4$ (CZGS) at a temperature above 800 °C^[20] or using non-equilibrium growth processes at 300 °C.^[21] Formation of mixed orthorhombic and tetragonal crystals was also recently presented by Niedenzu et al.^[22] These observations agree with the density functional theory (DFT) studies predicting smaller energy difference between KS and wurtzite phases in CZGS than that in CZTS.^[15]

Different elements, such as Si,^[23] Ge,^[24] Se,^[25] Cd,^[26] and Ag,^[27] can be introduced into CZTS to tune its structural and electronic properties. For instance, Cd and Ag are larger than the elements they substitute, Zn and Cu, respectively, which is

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suggested to improve the absorber quality by suppressing cation disorder in CZTS.^[28] Besides, the addition of Ag and Cd is predicted to alter the band edge position of KS.^[29] Ge incorporation on Sn site in CZTSe can also be effectively used due to its good miscibility, which is much better as compared with that for Si addition.^[18] Indeed, $\text{Cu}_2\text{ZnGe}_x\text{Sn}_{1-x}(\text{S}_y\text{Se}_{1-y})_4$ (CZGTSSe) absorbers demonstrate a high absorption coefficient of 10^4 cm^{-1} with a direct bandgap tunable from 1.0 to 1.9 eV,^[24,30,31] thus allowing its utilization in single-junction solar cells as well as in tandem devices. CZGTSSe with Ge concentration up to $x = 0.7$ and bandgap of 1.4 eV was fabricated with an efficiency of 6.8%. Giraldo et al.^[32] reported improved morphology, crystallinity, and possibly reduced SnSe loss with an optimized quantity of incorporated Ge. With all these efforts, the highest reported efficiency for Ge-incorporated KS $\text{Cu}_2\text{ZnGe}_x\text{Sn}_{1-x}\text{Se}_4$ (CZGTSe) has now reached 12.3%,^[13] which is only 0.3% lower than the current record for the CZTS-based devices.

Bandgap grading can be used as an effective approach to reduce back surface recombination.^[5] S/Se grading in CZTS was attempted in several reports by different fabrication methods,^[10,33,34] but no clear improvement was observed. This could be in part because the anion compositional grading is very challenging with some fabrication processes. Ross et al.^[35] reported that gradient formation in the case of S/Se is difficult to control due to rapid diffusion of chalcogens through the grain boundaries to the back contact and competing recrystallization. From this perspective, cationic substitution could be easier to control for the implementation of bandgap grading throughout the thickness of the absorber.

Very few reports are available on bandgap grading of CZTS with Ge, and more studies are needed to understand the material and solar cell properties as well as methods for fabrication of the desired gradients. Kim et al.^[36] used a method involving nanocrystals followed by spin coating to produce graded, Ge-based CZGTS. An efficiency of 6% was shown as compared to 3.4% for non-graded CZGTS. Schnabel et al.^[37] reported the incorporation of Ge into CZTSSe with bandgap tuning from S/Se substitution. The bandgap was widened from 1.5 to 1.7 eV, which led to higher V_{OC} but also increased V_{OC} deficit, probably due to increased interface recombination associated with the formation of a cliff-like conduction band offset at the absorber/buffer interface. Márquez et al.^[38] reported unintentional bandgap grading by Ge incorporation in CZTSe using sequential sputtering of metallic precursors. A 50 nm thick Ge layer was deposited on top of the metal precursor, but preferential Ge diffusion towards the back interface was observed after selenization. In a recent study, elemental targets were co-sputtered to fabricate CZGTSe devices with shallow Ge grading from both graded and stacked precursors.^[39] Unlike in the work by Márquez et al.,^[38] no preferential accumulation of Ge near the back contact was observed. However, no improvement in V_{OC} deficit or carrier collection was found. A steeper bandgap grading could be beneficial, and more control over Sn–Ge gradient formation in CZTS and CZTSSe is needed.

In this work, we report on one of the first attempts to use compound co-sputtering for fabrication of CZGTS thin films and formation of a steep Sn–Ge gradient of bi-layer precursors by depositing CZTS on top of CZGS. The influence of Ge content in homogenous CZGTS on material properties and the evolution

of the Sn/Ge gradient as a function of sulfurization time are studied. A comparison of CZGS thin films prepared by sputtering from Ge and GeS targets is also included to evaluate the influence of sulfur content on the material properties.

2. Results

2.1. Comparison of GeS and Ge Target

Figure 1a shows the grazing incidence X-ray diffraction (GIXRD) of CZ(GeS)S (with GeS target) and CZ(Ge)S (with Ge target) precursors and sulfurized samples. It should be noted that “CZ(GeS)S” and “CZ(Ge)S” are used as sample names in the context of comparing deposition from different targets. The GIXRD peaks in the precursors can be assigned to CZGS phase and Mo, as discussed later in connection with the CZGTS series (CZTS, $\text{Cu}_2\text{ZnGe}_{0.2}\text{Sn}_{0.8}\text{S}_4$, $\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$, and CZGS). The CZ(GeS)S precursor shows a very broad peak between $50^\circ < 2\theta < 60^\circ$, which may be due to the presence of mixed phases of wurtzite and KS phases. CZ(GeS)S did not recrystallize as opposed to CZ(Ge)S in which additional peaks belonging to the tetragonal structure (ICDD file 04-012-7580)^[40] appeared after sulfurization. The Raman scattering of sulfurized CZ(GeS)S and CZ(Ge)S is obtained using two different laser wavelengths, as shown in Figure 1b. The Raman signature of CZ(Ge)S matched very well with previous reports in CZGS.^[41]

The poor crystallinity of sulfurized CZ(GeS)S film can be assessed by the broad peaks in GIXRD along with broad diminished Raman peaks. This is also confirmed using scanning electron microscopy (SEM) imaging shown in Figure 2, where the columnar structure of the precursor grains persists for the CZ(GeS)S sample, whereas the CZ(Ge)S sample shows the expected recrystallized morphology. Repeated deposition and sulfurization of CZ(GeS)S precursors confirmed the poor crystallinity. It is possible that fine-tuning of the sputtering parameters or sulfurization process could promote recrystallization of CZ(GeS)S, but to keep previously optimized baseline conditions from CZTS for the CZGTS series, the Ge target was used for the experiments discussed in this article. The CZGS abbreviation is adopted for the samples with intended CZGS composition henceforth.

2.2. Uniform Precursors with Variation of Ge/(Ge + Sn) Ratio

In Table 1, the thickness of the films was determined from SEM cross sections, and the bandgap was determined from optical measurements of the annealed samples, whereas composition was obtained from the precursor films by X-ray fluorescence (XRF) calibrated using Rutherford backscattering (RBS). To demonstrate that uniform CZGTS with a wide range of Ge/(Ge + Sn) ratios can be prepared using our approach, a set of samples with different Ge contents (Table 1) were fabricated by co-sputtering. Copper-poor and zinc-rich CZTS absorbers have been found to be beneficial for the solar cell performance.^[42] Therefore, we fabricated CZTS, $\text{Cu}_2\text{ZnGe}_{0.2}\text{Sn}_{0.8}\text{S}_4$, $\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$, and CZGS thin films in this compositional range.

Figure 3a shows the GIXRD of precursor films. Only a few peaks corresponding to KS symmetry are perceived, similar to

Figure 1. a) GIXRD of precursors and sulfurized samples of CZ(GeS)S (with GeS target) and CZ(Ge)S (with Ge target). The peaks at 40.4° , 58.6° , and 73.8° correspond to Mo back contact. Raman measurement of sulfurized b) CZ(GeS)S and c) CZ(Ge)S observed under excitation wavelengths of 532 and 785 nm.

Figure 2. SEM cross-sectional imaging of a) CZ(Ge)S precursor and b) sulfurized CZ(Ge)S. Surface morphology of c) CZ(Ge)S precursor and d) sulfurized CZ(Ge)S. Cross-sectional imaging of e) CZ(GeS)S precursor and f) sulfurized CZ(GeS)S. Surface morphology of g) CZ(GeS)S precursor and h) sulfurized CZ(GeS)S.

previous studies of reactively sputtered CZTS at a low temperature along with one broad peak at about 52° ,^[45] which may reflect the presence of wurtzite phase. Moreover, the intensity

Table 1. List of samples showing absorbers thickness (sulfurized precursors), precursor composition, and bandgap (E_g).

Sample	Thickness [nm]	Cu/ (Sn + Ge)	Ge/ (Ge + Sn)	Zn/ (Cu + Sn + Ge)	E_g [eV]
$\text{Cu}_2\text{ZnSnS}_4$	880	1.94	0	0.36	1.57
$\text{Cu}_2\text{ZnGe}_{0.2}\text{Sn}_{0.8}\text{S}_4$	940	1.85	0.18	0.35	1.69
$\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$	840	1.95	0.38	0.39	1.73
$\text{Cu}_2\text{ZnGeS}_4$ (CZGS)	955	1.83	1.0	0.39	2.23
$\text{Cu}_2\text{ZnGeS}_4$ (CZ(GeS)S)	995	1.96	1.0	0.35	–

of this peak decreases with increasing concentration of Ge in CZGTS. The intense characteristic peaks of CZTS and CZGS are found at 28.3° and 29.0° , respectively. One unknown shoulder peak at 27.6° and three small consecutive peaks at 43.1° , 44.2° , and 45.5° marked with “*” are observed in CZGS. The double peak at 57.2° in the CZGS precursor agrees with the tetragonal CZGS structure (ICDD file 04-012-7580).^[40]

The crystallinity of the samples is improved after sulfurization (Figure 3b), and the characteristic peaks of CZGTS are verified against ICDD files of CZGS (04-012-7580)^[40] and CZTS (01-082-3166).^[43] This shift in GIXRD peaks towards higher 2θ values agrees with previous studies^[46] and is due to the replacement of Sn with the smaller Ge atom leading to shrinking of the lattice. There is no clear evidence of secondary phases in GIXRD, although some phases, such as ZnS , $\text{Zn}_{0.5}\text{Ge}_{0.25}\text{S}$,^[47] Cu_2GeS_3 (CGS),^[48] Cu_2SnS_3 (CTS),^[48] Cu_4SnS_4 ,^[49] and GeO_2 ,^[50,51] are difficult to distinguish due to the peak overlap. Therefore, the GIXRD measurement is not sufficient to evince dominance of single-phase tetragonal CZGTS. The fact that all precursor films

Figure 3. a) GIXRD of CZGTS precursors and b) sulfurized samples with different Ge concentrations ($\varphi = 1^\circ$). The peak positions are consistent with the XRD patterns of CZTS (ICDD 01-082-3166),^[43] CZGS (ICDD 04-012-7580),^[40] and Mo (ICDD 04-014-7435).^[44]

shown in Figure 3 recrystallize during annealing, in contrast to the CZ(GeS)S film in Figure 1, could imply that appearance of wurtzite phase in CZGS is more harmful than that in CZTS. This will be further discussed in connection to ab initio calculations later in the article and in the discussion section.

Raman measurements were carried out to further investigate the existence of secondary phases. Figure S1, Supporting Information, shows multi-wavelength Raman spectra of the CZGTS precursor series. No clear indications of different vibrational Raman modes are found under an excitation of 785 and 325 nm laser. The broad peak of the A^1 mode can be observed with the 633 nm laser for all samples from the CZGTS series except in CZGS where the peak intensity is significantly lower. The Raman signature of the CZGTS series is sharper with the indication of the A^2 mode under excitation by the 532 nm laser. The presence of secondary phases, such as CGS (321, 360, and 384 cm^{-1})^[52] and CTS (285 and 332 cm^{-1})^[53] cannot be excluded due to the broad Raman peaks of the precursors. In contrast, the presence of ZnS on surface of all precursors is not confirmed due to the absence of quasi-resonant excitations of ZnS vibrational modes under an excitation wavelength of 325 nm.^[54]

The lack of ZnS peaks on the surface of precursors agrees with previous studies of reactively sputtered CZTS precursors.^[53] Together with the GIXRD analysis showing the overlapping peaks from tetragonal CZTS, CTS, and ZnS, zinc-blende metastable phase could form within the sputtered precursor, as suggested by our previous findings. In this series, the same structure pattern is observed with increasing Ge content. The main difference occurred for the pure CZGS precursor, where the Raman scattering is almost featureless and where a few additional peaks are observed in GIXRD.

Figure 4 shows the Raman spectra of the sulfurized films. The selective wavelength resonance (or close) to electronic transitions of CZTS shows intense Raman mode, which makes this

technique very sensitive.^[56] Raman signature of the intense phonon symmetry mode blueshifted from Sn-like to Ge-like character with an increase in the Ge concentration. The phonon scattering modes of CZTS and CZGS were observed at $337\text{ (A}^1\text{)}$, $290\text{ (A}^2\text{)}\text{ cm}^{-1}$ and $360\text{ (A}^1\text{)}$, $295\text{ (A}^2\text{)}\text{ cm}^{-1}$, respectively.^[41] The evolution of asymmetric double peaks could be attributed to the presence of mixed CZGTS compositions in $\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$. The unknown peak at 263 cm^{-1} seen with a laser excitation of 633 nm for the $\text{Cu}_2\text{ZnGe}_{0.2}\text{Sn}_{0.8}\text{S}_4$ sample may belong to the tetrahedral GeO_x phase.^[57] The Raman vibrational A^1 mode of CZGS evolves into a broad and double peak with an increase in the Ge concentration, due to contribution of Raman vibrational A^1 modes of CZGS and CZTS. No secondary phases, such as Cu_{2-x}S , GeS_2 , CTS, CGS, and Cu_2Ge , except ZnS were found with different excitation wavelengths of laser in Raman spectrum.

The optical absorption of all the samples in the CZGTS series is shown in Figure S2, Supporting Information, and bandgap values are given in Table 1. Tauc plots were obtained by plotting $(ah\nu)^2$ versus the photon energy ($h\nu$), and extrapolation of the linear regions to the abscissa ($h\nu$ -axis) was performed to determine the direct optical bandgaps. As one can see, the bandgap increases with the Ge concentration as expected. The absorption coefficient α was obtained by reflectance (R) and transmittance (T) measurements using the following equation^[58,59]

$$\alpha = \frac{1}{t} \ln \frac{(1 - R^2)}{T} \quad (1)$$

where t is the thickness of the absorber film.

Figure 5 shows the surface morphology along with cross-sectional SEM of CZGTS samples with different Ge/(Ge + Sn) ratios. $\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$ precursor (Figure 5j,n) has the same morphology as CZTS, with columnar grains and faceted surface. The $\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$ sample is also similar to CZTS, but with

Figure 4. Raman spectra of sulfurized CZGTS with different excitation lasers. Raman peaks of CZTS at 290 cm^{-1} (A^2 mode), 337 cm^{-1} (A^1 mode) and CZGS at 295 cm^{-1} (A^2 mode), 360 cm^{-1} (A^1 mode) are observed under a laser excitation wavelength of a) 785, c) 633, and d) 532 nm. The plots are labeled with the corresponding excitation wavelength of the laser. The presence of ZnS is detected in Raman spectrum under an excitation wavelength of b) 325 nm.

a more rounded shape of the grains, whereas the CZGS sample differs in both the cross-sectional and top-view SEM. The morphology can be compared with the structure zone model (SZM) for the sputtered films as a function of the process parameters, such as Ar pressure and substrate temperature defined as T/T_m , where T_m is the melting temperature of the material.^[60] For CZTS, the structure agrees with zone 2, whereas for increasing Ge content, a transition to zone 1 is seen. This is characterized by the reduced crystallinity and featureless surface. The precursor structure of the CZGS sample sputtered with GeS target shown in Figure 2c resembles that of the precursors with lower Ge content. The former, however, appears to have lower surface roughness and less-defined columnar grains.

Sulfurization of the precursors led to increased grain size with overall grain growth being fastest in $\text{Cu}_2\text{ZnGe}_{0.2}\text{Sn}_{0.8}\text{S}_4$ among CZGTS series (Figure 5f). The crystallite size grew up to around $1\text{ }\mu\text{m}$ in case of $\text{Ge}/(\text{Ge} + \text{Sn}) = 0.2$ as compared with around $0.6\text{ }\mu\text{m}$ in CZTS. The surface of CZGS (Figure 5h) was observed to be covered with small bright grains, which are most likely made of ZnS (Table S1, Supporting Information).

To get a fundamental insight into the deposition and recrystallization of CZGTS precursors, we performed ab initio calculations of the alloy stability with respect to the composition in four competing phases: KS, SN, wurtzite-kesterite (WZ-KS), and wurtzite-stannite (WZ-SN). The obtained results shown in Figure 6a demonstrate that KS phase remains the most stable in the entire range of Sn–Ge compositions. Hence, KS is expected to dominate in stoichiometric CZGTS with all $\text{Ge}/(\text{Ge} + \text{Sn})$ ratios at equilibrium. The precursor deposition, however, is highly non-equilibrium process that may instead produce a mixture of phases if their energies are sufficiently

close. In this regard, our calculations reveal that the SN, WZ-KS, and WZ-SN phases of pristine CZTS are 2.87 , 6.99 , and $8.27\text{ meV atom}^{-1}$, respectively, higher in energy compared with the ground-state KS phase. Such small energy differences imply a possibility of concurrent growth of the orthorhombic and tetragonal phases in co-sputtered CZTS precursors. From the other side, the KS phase in pristine CZGS is followed in stability by WZ-KS, SN, and WZ-SN that are 4.33 , 4.48 , and $6.13\text{ meV atom}^{-1}$, respectively, higher in energy, in qualitative agreement with the previous study.^[15] Notably, while the energies of these phases are close enough to coexist in the precursors, there is an essential $2.66\text{ meV atom}^{-1}$ difference in the stability of WZ-KS in CZTS and CZGS. In a wider range of compositions, this difference translates into a clear tendency for stabilizing WZ-KS phase upon Ge alloying. Considering that WZ-KS and KS phases must be separated by an energy barrier that is naturally higher for phases with different lattice symmetries,^[61] the stabilization of WZ-KS phase can slow down recrystallization kinetics for the precursors with high $\text{Ge}/(\text{Ge} + \text{Sn})$. This mechanism explains why the broad GIXRD peak of wurtzite phase disappears after sulfurization of CZTS (Figure 3a) but not in $\text{CZ}(\text{GeS})\text{S}$ (Figure 1a) films. From this perspective, suppressing the formation of wurtzite phase in $\text{CZ}(\text{GeS})\text{S}$ precursor by using S-poor elemental Ge target (Figure 1a) could be an effective route to overcome the slow recrystallization problem in CZGS.

To realize homogeneous one-phase CZGTS absorbers, the alloys should be miscible in the first place. As can be seen in Figure 6b, the computed bowing parameter for the formation energy of KS phase is 8.94 eV atom^{-1} only, indicating good miscibility of Ge and Sn in this phase. This conclusion is better illustrated by a simplified phase diagram of CZGTS derived

Figure 5. SEM cross section of sulfurized a) CZTS, b) $\text{Cu}_2\text{ZnGe}_{0.2}\text{Sn}_{0.8}\text{S}_4$, c) $\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$, and d) CZGS. Surface morphology of e) CZTS, f) $\text{Cu}_2\text{ZnGe}_{0.2}\text{Sn}_{0.8}\text{S}_4$, g) $\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$, and h) CZGS. Cross section of precursors i) CZTS, j) $\text{Cu}_2\text{ZnGe}_{0.2}\text{Sn}_{0.8}\text{S}_4$, k) $\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$, and l) CZGS. Surface morphology of m) CZTS, n) $\text{Cu}_2\text{ZnGe}_{0.2}\text{Sn}_{0.8}\text{S}_4$, o) $\text{Cu}_2\text{ZnGe}_{0.4}\text{Sn}_{0.6}\text{S}_4$, and p) CZGS.

Figure 6. Stability of CZGTS alloys obtained from first-principles calculations. a) Computed enthalpies of mixing (markers) and parabolic fits (lines) for CZGTS alloys in four different phases: KS, SN, WZ-KS, and WZ-SN. b) Simplified phase diagram of KS CZGTS derived from the regular solution model using a fitted bowing parameter of $8.94 \text{ eV atom}^{-1}$.

using the regular solution model.^[62] As one can see, the consolute temperature of CZGTS alloy is 141 °C, which is significantly lower than the substrate temperatures used during sputtering (250 °C) and sulfurization (581 °C). It is noteworthy that a good miscibility in KS phase was also predicted for Ge and Sn in CZGTSe alloys.^[18] Furthermore, similarly, low bowing parameters of 9.25, 11.4, and 11.71 meV atom⁻¹ were computed for SN, WZ-KS, and WZ-SN, respectively, implying that good miscibility of CZTS-CZGS is a common feature of all four phases studies herein. Practically, such a good miscibility in KS phases opens up a possibility to form a desired Ge gradient within the CZGTS grains.

2.3. Sulfurization of CZTS/CZGS Bi-Layer Precursors

In an attempt to create a Ge gradient within the absorber, a CZTS(top)/CZGS(bottom) bi-layer was deposited and annealed in the presence of S for 2 (CZTS/CZGS_2), 6 (CZTS/CZGS_6), and 13 min (CZTS/CZGS_13). **Table 2** shows the composition, determined from XRF, and the thickness of the bi-layer precursors, determined from XRF counts calibrated by profilometer measurements on a set of precursor samples. The CZGS film is slightly copper-poor and zinc-rich as compared with the CZTS layer. GIXRD of bi-layer and all sulfurized absorbers (CZGTS grading) are shown in **Figure 7**.

The peak shifts toward higher angles with an increase in sulfurization time, from 47.5° for the 2 min sample to 47.6° for 13 min for the 204/220 peak. GIXRD peaks of CZTS/CZGS_2 are broader and less intense as compared with CZTS/CZGS_13, which is related to the poor crystallinity of the absorber after the short sulfurization time. The asymmetry of the peaks could be due to the presence of a compositional gradient from top to bottom.

Table 2. Thickness and composition of the CZTS/CZGS stack precursors.

Sample	Thickness [nm]	Cu/(Sn + Ge)	Ge/(Ge + Sn)	Zn/(Cu + Sn + Ge)
Cu ₂ ZnSnS ₄	240	1.86	0	0.33
Cu ₂ ZnGeS ₄	180	1.82	1.0	0.37

Figure 8. Raman signature of CZTS/CZGS_2, CZTS/CZGS_6, and CZTS/CZGS_13 measured with an excitation laser of 532 nm.

The characteristic peaks in GIXRD are initially dominated by the top layer of the film, which is Ge-free CZTS before sulfurization.

Figure 8 shows the Raman measurement of sulfurized CZGTS-grading samples under an excitation wavelength of 532 nm. In CZTS/CZGS_2, the A¹ mode of CZTS can be observed at 338 cm⁻¹, and the gradual peak shift toward higher wavenumbers can be seen with increasing sulfurization time. Other vibrational modes were not visible in this measurement. The full width at half maximum (FWHM) of this peak increases with increase in sulfurization time, which can also be compared with **Figure 4** where the peak broadening is observed for CZGTS alloy samples as well.

The distribution of elements in the CZGTS-grading series is investigated using glow discharge optical emission spectroscopy (GDOES), as shown in **Figure 9**. The initial Sn/Ge gradient gradually smears out as a function of sulfurization time and vanishes after 13 min. The slightly higher Zn content of the CZGS back layer shifts toward the front of the film already after 2 min sulfurization. The Zn concentration further increases at the surface after 13 min annealing. The Na signal is initially slightly

Figure 7. a) GIXRD at a grazing incidence of 1° for CZTS/CZGS_precursor, CZTS/CZGS_2, CZTS/CZGS_6, and CZTS/CZGS_13. b) Peak shift with sulfurization time for the reflection from (112) plane.

Figure 9. GDOES measurement of elemental depth profiles for Cu, Zn, Sn, Ge, S, Na, Mo, and O in a) CZTS/CZGS_precursor (bi-layer of CZTS on top of CZGS before sulfurization), b) CZTS/CZGS_2 (CZTS/CZGS annealed for 2 min), c) CZTS/CZGS_6 (CZTS/CZGS annealed for 6 min), and d) CZTS/CZGS_13 (CZTS/CZGS annealed for 13 min).

higher in the CZGS back layer and increases in the near-surface region as expected with sulfurization time.

Scanning transmission electron microscopy (STEM) images of the CZGTS-grading samples with varying annealing times are overlaid with energy dispersive X-ray spectroscopy (EDS) elemental mappings of Ge, Sn, and O in **Figure 10**. In CZTS/CZGS_2, Zn and Cu segregation can also be observed (Figure S3, Supporting Information). Ge and Sn interdiffused between CZTS and CZGS layers during sulfurization. Preferential diffusion of Ge through grain boundaries and Sn penetration into the grain interior are clearly visible in case of CZTS/CZGS_6.

Precipitates of GeO_x phase are present in the grain boundaries and especially at the triple points of grain boundaries, which could not be confirmed using GIXRD. A slightly higher oxygen concentration in the bottom part of the 2 and 6 min annealed absorbers was also seen in the GDOES profile (Figure 9). Ge and O concentrate in the same regions, primarily around voids, which could lead to the formation of GeO_x phase. Bär et al.^[63] reported the possible oxidation of Zn, Sn, and S when Cu-poor CZTS is air exposed. The oxidation near the back contact may occur during the preparation of CZTS/CZGS lamella with focused ion beam (FIB). The oxidation is more likely for the samples grown from elemental Ge target, which are naturally more reactive than those grown from GeS source, although the oxidation of GeS was also found in ambient atmosphere.^[64,65] Moreover, O- and Ge-enriched surfaces in STEM images could represent the oxidation of other elements along with Ge. Oxidation may also occur during the sulfurization step if there is some leakage of oxygen into the annealing chamber.^[66] Optimal control of oxidation of CZTS thin film may lead to improved solar cell absorber,^[13] and further studies of the influence from Ge content on the post air annealing are needed.

Figure 10. STEM/EDS of CZGTS-grading samples sulfurized for different durations. CZTS/CZGS_2, CZTS/CZGS_6, and CZTS/CZGS_13 were annealed for 2, 6, and 13 min, respectively. Germanium diffusion through the grain boundaries and tin diffusion into the grain interior are observed.

The thickness of CZTS/CZGS_13 films slightly decreased to 390 nm as compared to 400 nm for CZTS/CZGS_2 and CZTS/CZGS_6 films. A MoS₂ layer with ≈ 100 nm thickness can be seen after 13 min sulfurization in Figure S4, Supporting Information.

3. Discussion

3.1. Precursor Properties

For the CZGTS precursors series, GIXRD showed the expected evolution of (112) reflection toward higher 2θ values with an increase in the Ge content. The broad peak observed at $50^\circ < 2\theta < 60^\circ$ decreased with an increase in the Ge content, which may also be related to the S content as shown by the comparison between CZ(GeS)S and CZ(Ge)S. For instance, reduced availability of sulfur in the target could suppress the growth of wurtzite phase during sputtering and, thus, promote recrystallization of the precursors. This broad peak has been previously observed in our CZTS films using GIXRD for precursors sputtered at higher temperatures, but also for sputtered ZnS films. In the case of reactive sputtering of ZnS in an industrial sputtering system, a more intense and narrower peak at 52° was reported together with other peaks that agree with the wurtzite ZnS phase.^[66] The appearance of non-equilibrium phases is common in sputtering, and in this case, it is possible that inclusions of wurtzite CZTS are formed in precursors under certain conditions. The reason why only one peak is observed is not clear. One explanation could be related to the strong orientation of the sputtered films. For GIXRD, only the randomly oriented parts of the film are observed together with grains oriented perpendicular to the diffraction normal. In Bragg–Brentano geometry, the overall intensity is reduced due to the smaller diffraction volume, and only the strong peaks are observed.

As discussed, CZTS may exist in different phases, that is, KS, SN, WZ-KS, and WZ-SN. The computed energy difference between the ground-state KS and wurtzite phases is on the order of meV atom^{-1} , which suggests that the concurrent growth of several phases is possible with highly non-equilibrium growth methods, such as sputtering. Indeed, wurtzite CZTS nanocrystals have been synthesized and studied,^[67] and the rapid recrystallization from metastable wurtzite to KS has been suggested as a promising route to large-grained CZTS at lower temperature.^[68] However, as the energy difference between the KS and WZ-KS phases decreases upon Ge alloying, as shown using the DFT, herein, the recrystallization kinetic can be slower in Ge-rich samples. The coexistence of mixed crystals of orthorhombic and tetragonal structure in CZGS may also affect GIXRD spectra of CZGTS. Wurtzite CZGS or CZTS can be present in stacking faults of KS phase.^[69,70] The broad peak may also be due to small agglomerates of wurtzite ZnS, but this effect cannot be observed in Raman spectrum of precursors using the 325 nm laser. The broad peak for the precursors may also represent Cu–Sn–S phases, which can be present during non-equilibrium deposition conditions of co-sputtering. A thin (around 65 nm) layer of MoS₂ grew during sulfurization of CZGTS sample, which may cause the presence of GIXRD broad peak, but no MoS₂ layer is observed from SEM in the precursors.

3.2. Properties after Sulfurization

Multi-wavelength Raman showed intense peaks corresponding to vibrational modes of CZTS, CZGS, and CZGTS absorbers. With an increase in the Ge concentration in CZGTS, the blueshifted A¹ mode becomes broader and evolves into a double peak, as also shown by Chen et al.^[46] ZnS might segregate in bulk of the precursor film and recrystallize near the surface during sulfurization of CZGTS films. The strong ZnS Raman signal is in agreement with the presence of this secondary phase on the surface, which can be confirmed with SEM/EDS as bright ZnS grains on top of CZGS. Cu₂ZnGe_{0.2}Sn_{0.8}S₄ is observed to have slightly larger grains as compared with CZGTS samples with the other Ge concentrations. A small broad Raman peak can be observed at 384 cm^{-1} in CZGS, which may be due to a combination of vibrational modes of CGS (384 cm^{-1})^[52] and CZGS (381 cm^{-1}) under an excitation of 532, 633, and 785 nm lasers. The broadness of this peak may also be due to convolution of Raman signal from both phases.

3.3. Gradient Formation

The formation of Ge gradient was attempted using sulfurization of CZTS/CZGS stack. In principle, a smooth gradient in CZGTS absorbers should be possible to realize owing to good miscibility of the alloy shown with first-principles calculations. Indeed, Ge and Sn interdiffusion between the CZTS and CZGS layers begins as soon as the sulfurization is started. GIXRD peaks became broader in CZTS/CZGS_2 and CZTS/CZGS_6 samples due to a collective contribution of recrystallized crystals in different CZTS and CZGS layers, in combination with a Sn–Ge gradient forming between these samples. In our case, the graded composition after 2 and 6 min is accompanied by a large-grained top layer and a small-grained bottom layer. It remains to be investigated if such back-layer morphology is detrimental to the device performance, but we note that short annealing for 1 min of CZTS has led to higher voltage and efficiency as compared with 13 min annealing using our process, despite the smaller grains.^[71] This implies that the short annealing times needed here to maintain a Ge/Sn gradient can be compatible with, and even advantageous for, obtaining good device performance. For the non-graded film after 13 min sulfurization, the composition approximated from the GIXRD peak shift is around $\text{Ge}/(\text{Ge} + \text{Sn}) = 0.3$. Raman peak of CZTS/CZGS_13 occurred at 342 cm^{-1} that is between A¹ mode of Cu₂ZnGe_{0.2}Sn_{0.8}S₄ and Cu₂ZnGe_{0.4}Sn_{0.6}S₄, which also indicates a Ge composition close to 0.3. This value is slightly lower than the composition estimated from the thickness of the CZTS and CZGS precursor layers in Table 2, but this difference can be rationalized, considering that the density of the precursors can also differ.

The relative elemental composition of CZTS/CZGS precursor deduced by GDOES showed that CZGS contains less Cu, S, and O and more Zn as compared to CZTS layer as confirmed by XRF in Table 2. However, it should be acknowledged that the depth resolution of GDOES depends on roughness, pinholes, matrix of elements in the sample, and so on. More oxygen near the surface seen in GDOES spectra of all the samples may be due to oxidation. Zn amount increased near the surface and

decreased toward the Mo layer as soon as the sulfurization started. Ge and Na concentrations increased in the near-surface regions of CZTS/CZGS_2 and CZTS/CZGS_6, whereas the O content increased in the CZGS layer. The original Sn and Ge gradients vanished in the CZTS/CZGS_13 samples. The indications of Zn and Na segregating on the surface, as well as Cu accumulation near the back contact, were also observed after the 13 min anneal.

The interdiffusion of Ge and Sn can occur through various competing mechanisms.^[72] In general, atoms and molecules diffuse much faster through grain boundaries in polycrystalline materials,^[73] although the ratio between the grain boundary to bulk diffusion coefficients depends on the diffusing species. Indeed, as seen from the EDS mappings on the stacks after 2 and 6 min anneals, Ge diffuses faster through the grain boundaries as compared with the grain interior, whereas Sn readily penetrates into the grains. Furthermore, Ge may be present on the surface of CZTS, which could cause the blueshift of the Raman signal. Zn seems to be present in the form of particles in partially crystallized CZTS/CZGS_2 sample. Phase segregation seems to occur, and ZnS phase rises to the surface of CZGTS with sulfurization time. Such a complex character of interdiffusion makes it difficult to fabricate a smooth concentration gradient in polycrystalline CZGTS. Whether the type of gradient obtained in this study is beneficial for reduced back contact recombination remains to be studied.

4. Conclusion

In this work, a two-step process to fabricate compositionally graded CZTS with Ge incorporation was demonstrated. The dependence of bandgap on Ge content in CZGTS was revealed by analyzing CZGTS series with different Ge/(Ge + Sn) ratios, indicating a possibility of bandgap profiling in the compositionally graded films. The impact of Ge content on the film properties was investigated using GIXRD, Raman, and SEM. The influence of S content on the deposition and recrystallization of the precursors was also explored by comparing the films grown using elemental Ge and GeS targets. A distinct GIXRD peak was observed at about 52° for the precursors deposited from the sulfide targets and attributed to the wurtzite phase of CZGTS. The first-principles calculations revealed that wurtzite phases have relatively low formation energy, suggesting that the crystallization of these phases is possible during sputtering. Furthermore, the WZ-KS phase was found to be more stable in CZGS than in CZTS, implying that the presence of this phase in the Ge-rich precursors may suppress the recrystallization. Thus, lower crystallinity of the precursors grown from Ge target could lead to a better quality of the absorber. No Ge-containing secondary phases were found, except for GeO_x near the back contact of the film. A steep compositional Sn–Ge gradient was obtained after optimized sulfurization of co-sputtered bi-layer precursor. The Sn–Ge gradient evolved by Ge diffusing through the grain boundaries and Sn diffusing into the grains. STEM/EDS showed oxidation of grain boundaries near the back contact. Further investigations are needed to explore the effect of bandgap grading on performance of the compositionally graded solar cells.

5. Experimental Section

Absorber Fabrication: Back contact Mo with a thickness of around 300 nm was deposited on soda lime glass by direct current (DC) sputtering from metal Mo target. The Mo-coated glass substrates were cut into square pieces of dimension 2.5 cm × 2.5 cm. CZGTS samples with four compositions (CZTS, Cu₂ZnGe_{0.2}Sn_{0.8}S₄, Cu₂ZnGe_{0.4}Sn_{0.6}S₄, and CZGS) were prepared by radio frequency (RF)/DC magnetron co-sputtering (Kurt J. Lesker RF/DC magnetron sputtering), as shown in Table 1. The four targets of CuS (purity of 99.99%), SnS (purity of 99.99%), ZnS (purity of 99.99%), and Ge (purity of 99.99%) or GeS (purity of 99.99%) were co-sputtered in an Ar pressure of 4 × 10^{−3} torr, keeping the substrates at 250 °C. The substrate holder was rotated at 20 rpm (rotations per minute) to achieve a uniform composition of CZGTS. One substrate was placed in the center of the substrate holder for measurement of elemental composition using XRF.^[74] After the deposition of the precursors, the films were sulfurized in a pyrolytic carbon-coated graphite box with 40 mg sulfur under a pressure of 350 torr Ar at 581 °C for 13 min. This sulfurization process was previously established for CZTS.

CZGS thin films were fabricated using two different sputtering targets: Ge or GeS. The bi-layer precursors for the compositionally graded samples (CZGTS grading) were fabricated by depositing CZTS layer on top of CZGS layer using co-sputtering from the elemental Ge target. CZGS samples were air exposed before depositing CZTS to measure the composition of the reference sample. The co-sputtered precursors were sulfurized for 2 (CZTS/CZGS_2), 6 (CZTS/CZGS_6), and 13 min (CZTS/CZGS_13) using the same sulfurization conditions as described earlier to investigate the formation of a Sn–Ge gradient throughout the thickness of the film.

Characterization: The cation composition of different films was measured using XRF in a PANalytical Epsilon-5 system calibrated using RBS. The composition of all the precursor films is presented in Table 1. The polycrystalline structure of the films was characterized by GIXRD in Siemens D5000 mirror diffractometer with Cu Kα radiation (1.54 Å) and a grazing incidence angle (φ) of 1°. The multi-wavelength Raman spectrum was recorded in a Renishaw inVia Raman scattering system using a laser excitation of 325, 532, 633, and 785 nm. This characterization was surface-sensitive with an estimated penetration depth between 20 and 700 nm depending on the laser wavelength. The transmittance and reflectance spectra were measured on PVE300 system equipped with integrating sphere and monochromatic light source. The light generated from xenon and halogen lamps was passed through monochromator to obtain monochromated light. The Si/InGaAs detector with a spectral range of 300–1700 nm was used for these measurements.

The film thicknesses of annealed CZGTS samples, surface morphology, and cross section of as-deposited and absorbers were measured using SEM in a Zeiss LEO 1550 system equipped with field-emission gun. The elemental profiles in the bi-layer precursor and CZGTS-grading series were investigated using GDOES measured with a Spectruma Analytik GDA 750HR analyzer with Ar as sputtering gas. The film thickness of bi-layer precursors was determined from XRF counts by comparing with reference samples. Cross-sectional lamellas were prepared with dual beam focused ion FEI DB235 FIB/SEM and imaged with FEI Titan Themis 200.

First-Principles Calculations: The first-principles calculations were performed within the DFT as implemented in Vienna ab initio simulation package (VASP).^[75–77] The projector augmented wave (PAW) pseudopotentials^[78,79] with Cu 3d¹⁰4s¹, Zn 3d¹⁰4s², Sn 4d¹⁰5s²5p², Ge 3d¹⁰4s²4p², and S 3s²3p⁴ valence electron configurations were used for the analysis. Perdew–Burke–Ernzerhof (PBE) functional was chosen for the study.^[80] The energy cutoff was set to 350 eV, and the ionic relaxations were preformed until reaching 0.01 eV Å^{−1} threshold for the atomic forces. The supercells consisting of 216 and 128 atoms were used to analyze the alloys in the tetragonal and orthorhombic phases, respectively. The alloy supercells were generated by special quasi-random structure (SQS) algorithm^[81] as implemented in the alloy-theoretic automated toolkit (ATAT) package.^[82] The lattice parameters for the alloy supercells were fixed, following Vegard's law using the optimized primitive cells of the pristine compounds. For each composition point presented in Figure 6a, the energy values represent average for three non-equivalent quasi-random

supercells. For all the supercell calculations, Γ -centered $2 \times 2 \times 2$ Monkhorst–Pack k-point grids were generated.^[83] From the initial calculations on CZTS and CZGS, this k-point density was found to yield 1–2 meV atom⁻¹ energy error on the related phase stabilities. To correct for this inaccuracy, a linear energy shift was first obtained from the energy calculations on primitive cells of CZTS and CZGS phases (8 atoms for the tetragonal and 16 atoms for the orthorhombic systems) using $8 \times 8 \times 8$ k-point grids and added to the total energies of the alloy supercells. The simplified phase diagram was constructed using the regular solution model.^[62]

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Keywords

chalcogenide, co-sputtering, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), Sn–Ge gradient, grain boundaries, wurtzite- $\text{Cu}_2\text{ZnGe}_x\text{Sn}_{1-x}\text{S}_4$

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Additional Information

Germanium incorporation in $\text{Cu}_2\text{ZnSnS}_4$ and formation of a Sn-Ge gradient

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Figure S1 Raman spectra of CZGTS precursors with different excitation lasers. Broad peaks due to contribution of Raman vibrational modes of CZTS at 290 and 337 cm^{-1} can be observed under the laser excitation wavelengths of (a) 785, (c) 633 and (d) 532 nm. The plots are labelled with the corresponding excitation wavelength of the laser. Raman signature of CZGS is very weak showing no sign of A^1 mode. There is no sign of ZnS with excitation of (b) 325 nm laser.

Figure S2 Tauc plots of CZGTS series. An increase in band gap is observed with increase in Ge concentration. Band gaps of CZTS, CZG_{0.2}T_{0.8}S, CZG_{0.4}T_{0.6}S and CZGS are found to be 1.57, 1.69, 1.73 and 2.23 eV respectively.

The band gap of CZGTS series is comparable to the band gap obtained in other reports.^[1,2]

Table S1 EDS composition table for the bright grains in Cu₂ZnGeS₄ film shown in **Figure 5**

(h).

Elements in CZGS	S (at%)	Cu (at%)	Zn (at%)	Ge (at%)
Large ZnS grain	50.02	17.14	24.37	8.47
Small ZnS grain	50.27	16.90	24.84	7.98

Figure S3 (a) EDS overlay of Zn and Cu on STEM of CZTS/CZGS_6 (annealed for 6 minutes) (b) CZTS/CZGS_13 (annealed for 13 minutes). Zn and Cu segregation can be observed.

Figure S4 Evolution of MoS₂ layer with annealing time.

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