Evolution of $\text{Cu}_2\text{ZnSnS}_4$ during Non-equilibrium Annealing with Quasi-in-situ Monitoring of Sulfur Partial Pressure

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ABSTRACT: Chalcogen based materials like $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) have drawn extensive attention for applications such as photovoltaics and water splitting. However, inability to monitor the sulfur partial pressure (P_{S_2}) during non-equilibrium annealing process at high temperature complicates the synthesis of CZTS with controlled optoelectronic properties. Here we demonstrated that P_{S_2} can be monitored by investigating the Sn-S phase transformation. We showed that P_{S_2} drops considerably over the annealing time, causing gradual alterations in CZTS: i) a change in defect type; ii) evolution of ZnS and Sn_xS_y phases. With additional ordering treatment, we observed that the low room temperature photoluminescence energy usually seen in CZTS can result from insufficient P_{S_2} during annealing. It is proven that remarkable V_{oc} beyond 700 mV for solar cells with non-optimal CdS buffer can be repeatedly achieved when CZTS is prepared under sufficiently high P_{S_2} . An ordering treatment before CdS deposition can further improve V_{oc} to 783 mV.

Introduction

The kesterite based materials $\text{Cu}_2\text{ZnSnS}(\text{Se})_4$ (CZTS(e)) have inspired considerable research in recent years. In addition to having all earth-abundant components, the suitable optical properties¹⁻² and tunability of the semiconducting properties by alloying various elements³⁻⁵ are promising features for developing sustainable photovoltaic technology.⁶⁻⁷ To produce CZTS thin films, the superior route by far is the two-step process, i.e. precursor deposition followed by a thermal treatment, which leads to a 12.7% record CZTSSe solar cell.⁸

The success of high temperature thermal treatment originates from use of a chalcogen atmosphere, which intends to prevent CZTS surface decomposition, shown by Reaction 1 in Table 1. As further noted from Reaction 2 in Table 1, CZTS instability actually can be driven by the possible decomposition of the SnS_2 binary compound. SnS_2 is sensitive to the S partial pressure (P_{S_2}), owing to the ability of Sn to change its oxidation state from (IV) to (II). A decrease in P_{S_2} can lead SnS_2 to transform to phases like Sn_2S_3 and SnS, as described by Reaction 3 in Table 1.⁹ In a similar manner, the Sn sub-lattice in CZTS tends to collapse as a result of reduction of Sn(IV) to Sn(II). This implies that effective mastery of P_{S_2} is one of the paramount challenges in CZTS synthesis. Nowadays elemental S is increasingly favored over toxic H_2S as a mean to supply chalcogen vapor, and various feeding methods in the thermal process are reported.¹⁰⁻¹⁶

Nevertheless, an extreme difficulty in controlling P_{S_2} lies in the problem of ensuring/measuring the actual P_{S_2} during the thermal treatment. This also inhibits a detailed understanding of the chemistry of the S-CZTS reactions (e.g. decomposition) that may occur. Sulfur is highly volatile, and the sulfurization or the chalcogen-containing annealing

process to synthesize CZTS is usually carried out under non-equilibrium conditions. For example, i) the evolution of the proportions of different allotropes of the chalcogen vapor (S_2 , S_4 , S_6 and S_8) leads to a fluctuation of the reactivity of the vapor environment; ii) pressure and thermal gradients in the annealing furnace due to process setup (such as gas flow, cold walls, volume change of the container etc.) create conditions that change over the duration of the anneal, which results in an unknown P_{S_2} reaching the CZTS surface. Consequently, there is a demand for “in situ” information to gain an in-depth understanding of this type of thin film growth.

In this work, we will provide a solution to monitor P_{S_2} during CZTS synthesis by utilizing the step-wise Sn-S phase transformation from SnS_2 to Sn_2S_3 to SnS. By annealing the CZTS film together with a SnS_2 monitoring film, we can acquire quasi-in-situ information of P_{S_2} from the resulting Sn-S phase and then correlate this to CZTS synthesis. We showed that P_{S_2} is highly dynamic over a short annealing time due to a rapid loss from the reaction zone. We also showed that this estimated P_{S_2} can be correlated well with the variation in material quality of the CZTS film under identical annealing processes, in terms of secondary phase formation as well as the evolution of defects in CZTS. The results suggested that the P_{S_2} , rather than the dwell time, is in fact the controlling variable for CZTS properties in non-equilibrium annealing, insofar as the dwell time is mainly responsible for determining the P_{S_2} , whereas the important reactions occur rapidly in response to changes in P_{S_2} . We performed Raman scattering with a multi wavelength setup and x-ray diffraction to demonstrate that ZnS and Sn-S compounds are the main secondary phases in the annealed Cu-poor, Zn-rich CZTS films. We observed from near resonant Raman scattering (NR-Raman) that the defect types in CZTS¹⁷ could

Table 1. Chemical reactions in Cu₂ZnSnS₄ and SnS₂ films during Annealing

	Chemical Reaction	Remark
Reaction 1	$\text{Cu}_2\text{ZnSnS}_4(\text{s}) \rightleftharpoons \text{Cu}_2\text{S}(\text{s}) + \text{ZnS}(\text{s}) + \text{SnS}(\text{s}) + 1/2\text{S}_2(\text{g}); \quad \text{SnS}(\text{s}) \rightleftharpoons \text{SnS}(\text{g})$	CZTS decomposition process
Reaction 2	$\text{Cu}_2\text{ZnSnS}_4(\text{s}) \rightleftharpoons \text{Cu}_2\text{S}(\text{s}) + \text{ZnS}(\text{s}) + \text{SnS}_2(\text{s})$	Formation of CZTS compound
Reaction 3	$2\text{SnS}_2(\text{s}) \rightleftharpoons \text{Sn}_2\text{S}_3(\text{s}) + 1/2\text{S}_2(\text{g}); \quad \text{Sn}_2\text{S}_3 \rightleftharpoons 2\text{SnS}(\text{s}) + 1/2\text{S}_2(\text{g})$	Sn-S phase transformation

convert from (A+B)-type (A type refers to the ($\text{V}_{\text{Cu}} + \text{Zn}_{\text{Cu}}$) defect pair and B-type refers to the ($2\text{Zn}_{\text{Cu}} + \text{Zn}_{\text{Sn}}$) defect pair) to nearly B-type CZTS as P_{S_2} declines, leading to a red shift of the room temperature photoluminescence (RT-PL) energy. Eventually it was demonstrated that sufficiently high P_{S_2} is essential for defect control in CZTS, and we managed to acquire V_{oc} above 700 mV (700-730 mV) for solar cell devices with over 6% power conversion efficiency (PCE). The strategy presented in this work to monitor the chalcogen partial pressure opens a new path for understanding and efficiently tailoring the growth of chalcogen-based materials in general for better controlled opto-electronic properties.

Experimental

Sputtering process. Sn-S and Cu-Zn-Sn-S precursor films were deposited onto 350 nm Mo back contacts prepared by DC sputtering on soda lime glass (SLG) substrates. 250 nm thick SnS₂ films were reactively sputtered in pure H₂S from a Sn target in a Von Ardenne system.¹⁸ 900 nm thick Cu-Zn-Sn-S precursor films were co-sputtered in a Kurt J. Lesker system from 3-inch CuS, ZnS and SnS targets (CuS: pulsed DC, 1.57 W/cm², SnS: pulsed DC, 3.20 W/cm², ZnS: RF, 0.52 W/cm²). The base pressure was below 10⁻⁵ Pa, and sputtering was done under 0.7 Pa of Ar flowing at 50 sccm. The substrate holder was kept at ~250 °C during the deposition. Eight identical Cu-Zn-Sn-S films could be prepared in one deposition process.

Annealing process. The precursor films (in each case, one 2.5×2.5 cm² CZTS/Mo/SLG sample and one 1×1 cm² SnS₂/Mo/SLG sample) were loaded into a pyrolytic-carbon-coated graphite box (GB) of 2.5×5 cm² size along with ~40 mg elemental sulfur. The GB is closed with a lid of the same material, **with a 2 mm-in-diameter hole**, which allows the box to remove the air prior to annealing (and which also allows S vapor to leak during the anneal). The precursors were then annealed in a tube furnace system composed of a load-lock, a water-cooled cold zone and a hot zone. After loading, the sample plate is located in the cold zone. A fast ramping thermal process can be realized by transferring the samples from the cold zone to the pre-heated hot zone. Sample temperature is recorded by a thermocouple embedded into sample holder. Samples were annealed at about 580 °C in a static Ar environment (46 kPa) with different dwell times to investigate the evolution of the P_{S_2} . Once the dwell is over, the sample plate is immediately withdrawn to the cold zone for rapid cooling. Before starting the thermal process, the GB was firstly cleaned in low vacuum at 600 °C for 10 h under a constant Ar flow

to eliminate possible adsorbed molecules from previous processes. The average ramping and cooling rates are about 5.5 K/s and 0.2 K/s, respectively. It needs to be remarked that nominal 0 min annealing means that the samples were rapidly removed to the cooling zone as soon as it reached the annealing temperature. In this work, the annealing time is the only experimental variable. The samples are named based on the material and the annealing time. For example, "C1" denotes CZTS annealed for 1 min while "S13" denotes SnS₂ annealed for 13 min. To investigate the potential influence of the SnS₂ film on the CZTS film during the same annealing process, CZTS samples were prepared without introducing SnS₂ film. C1R was annealed for 1 min as the reference and C13R was annealed for 13 min (C13R is our baseline reference process to fabricate solar cells¹⁹). X-ray fluorescence (XRF, PANalytical Epsilon 5) confirmed that the average composition of all annealed CZTS films does not vary from the precursor film, giving Cu/Sn~1.9 and Zn/Sn~1.0.

Solar cell fabrication. To continue the fabrication of solar cells, the annealed CZTS films were further processed with a chemical bath deposited CdS (~50 nm), RF sputtered intrinsic ZnO (~80 nm) and Al doped ZnO layers (~210 nm). Lastly, Ni/Al/Ni metal grid was deposited on top of the window layer for contact. The solar cell of 0.5 cm² total area was defined by the mechanical scribing.

Material characterization. Scanning Electron Microscopy (SEM, LEO 1550) was performed at 5 kV accelerating voltage. Phases in the films were identified using Raman scattering (Renishaw inVia system with 785 nm, 532 nm and 325 nm excitation wavelengths), as well as x-ray diffraction (XRD). XRD (Siemens D5000) measured with Bragg-Brentano focusing geometry is compared to grazing incidence x-ray diffraction (GIXRD) at 1° incidence angle in parallel beam geometry. Energy dispersive x-ray spectroscopy (EDS, Oxford instrument) was operated with 5 kV and 12 kV accelerating voltage on Sn-S and CZTS films, respectively.

Device characterization. Devices were characterized by illuminated current-voltage (J-V) characteristics and external quantum efficiency (EQE). The EQE setup was calibrated by an externally calibrated Hamamatsu Si solar cell. The illuminated J-V characteristics were determined from one sun illumination simulator (Newport, class ABA). The current derived from illuminated J-V characteristics was calibrated by the calculated current from the integrated QE with a standard AM1.5 solar spectrum, considering 2.5% shadow area from the grid contact.

Figure 1. (a) GIXRD of the Sn-S film as a function of the annealing time; (XXX-XXXX) presents the chosen PDF card, and respective dash line is drawn for the guidance of the peak identifications. (b) Contour plot of the Raman spectra of the annealed Sn-S film as a function of annealing time, intensity of individual Raman spectrum has been normalized. The specific Raman scattering of each sample can be seen in (Figure S1). (c) Raman scattering on various spots of the 5 min annealed Sn-S film, the color of the Raman spectrum corresponds to the respective dot on the optical image in the inset. (d) S/Sn ratio, determined by EDS, of the annealed Sn-S film, and the color lines guide the S/Sn ratio of possible Sn-S phases accordingly. The black sphere represents the precursor. (e) Pressure-temperature phase diagram of Sn-S system,⁹ and the boundary of figures (d) and (e) represents the performed annealing temperature at 580 °C in this work.

Results and discussion

Monitoring P_{S_2} from time resolved Sn-S phase transformation. Figure 1a presents the evolution of the GIXRD pattern of reactively sputtered SnS_2 films annealed with different durations in our CZTS anneal process. It is apparent that the polycrystalline SnS_2 precursor (SP-precursor) had a hexagonal structure (#023-0677). Once the annealing began (S0), the SnS_2 film was immediately recrystallized, with peaks at 28.3° (100), 32.2° (101), 50.1° (110) and 52.5° (111) vanishing while peaks at 41.9° (102), 54.9° (103) and 77.6° (203) were strengthened. The GIXRD features changed considerably after annealing the SnS_2 film for 5 min. The Sn-S film (S5) can be identified as a mixture of hexagonal SnS_2 (#023-0677), orthorhombic Sn_2S_3 (#014-0619) and orthorhombic SnS (#075-0925) phases. When extending the annealing beyond 13 min (S13, S40), only the orthorhombic SnS phase can be confirmed. Since GIXRD only provides average structural information, we performed confocal micro-Raman for local examination on the annealed Sn-S film. As displayed in Figure 1b, the path of the Sn-S phase transformation indicated by the contour plot of the Raman spectra is in accordance with the GIXRD in Figure 1a. It can be noted that the initial SnS_2 phase (315

cm^{-1}) was stable until the annealing time reached 5 min.²⁰ Upon 5 min annealing, SnS_2 started to transform to Sn_2S_3 (233 cm^{-1} , 257 cm^{-1} and 307 cm^{-1}) and SnS (156 cm^{-1} , 185 cm^{-1} and 221 cm^{-1}).²⁰ Beyond 13 min of annealing, SnS_2 had completely converted to SnS. Another observation with increased annealing time is the disappearance of the MoS_x phase (286 cm^{-1} , 383 cm^{-1} and 408 cm^{-1})²¹ that forms at the Mo/Sn-S interface, likely due higher absorption of SnS to the Raman excitation wavelength (532 nm) compared to that of SnS_2 .²²⁻²³ Besides, we find that the Raman results of S5 are interesting, because a lateral structural inhomogeneity can be optically visible (inset in Figure 1c). By a series of Raman measurements on S5, we could detect that the film showed large local variation in the three Sn-S phases, rather than the phases existing in a layered structure (SnS_2 (rear)/ Sn_2S_3 /SnS(front)), as could be expected for S loss from the surface. After measuring Raman over 20 spots, we observed that majority of the film shows the co-existence of SnS and SnS_2 phases. Thereupon we hypothesize that the transition from SnS_2 , Sn_2S_3 to SnS is fast, which possibly stems from the narrow limit of S partial pressure to stabilize Sn_2S_3 phase.⁹ This indicates a sulfur loss process could have already occurred in the Sn-S film during the 5 min anneal. Figure 1d shows the evolution of S content in

the annealed Sn-S films, which is derived from EDS. The S/Sn ratio can be correlated well with the phases verified by Raman and GIXRD at different annealing stages, as labeled in Figure 1d. It can also be correlated with the pressure-temperature phase diagram of the Sn-S system, as outlined in Figure 1e. We noticed that the S/Sn ratio (initially ~2) was reduced, and was saturated after annealing Sn-S film above 5 min ($S/Sn \leq 1.5$). Since the maximal S/Sn ratio is set by the SnS_2 phase, we can ensure that P_{S_2} is adequate to preserve the oxidation state of Sn(IV) in SnS_2 film when the anneal time is less than 3 min.

The results in Figure 1 strongly imply that in addition to the dwell time, the P_{S_2} is another critical factor that shows a dynamic feature in the non-equilibrium annealing. It is notable that the required P_{S_2} to prevent S loss from SnS_2 at 580 °C is about 30 mbar in Figure 1e. Comparing to the saturated vapor pressure P_{S_2} (~5 bar) that is assumed to be provided by the loaded sulfur excess mass (40 mg), it is surprising to find that this expected high P_{S_2} is lost very quickly (already occurred only after 3 min dwell time) in the non-equilibrium annealing process. This implies that either the leak rate of sulfur vapor from the closed graphite box during the annealing process is considerably high, or the behavior of P_{S_2} predicted from the thermodynamic data used for Figure 1e is not applicable to this case. The former one could be limited by the process setup. The reason for the latter one could be that the assumption that the sulfur vapor only contains S_2 molecules is invalid anymore at high S pressure.²⁴ We suggest that the ability of sulfur vapor to preserve Sn(IV) may depend on the process setup, as well as the constitution of sulfur vapor, which is temperature and pressure dependent.

To ensure a sufficient P_{S_2} for the annealing process, it is apparent that efforts should be made to improve the anneal system, such as the graphite box design. With the observed dynamic feature of P_{S_2} , we will now start to investigate the influence of the time resolved P_{S_2} on CZTS.

Time resolved grain growth and chemical composition of CZTS films. Figure 2 presents cross section images of all studied CZTS films prepared together with the SnS_2 films. The sample C0 does not show significant difference from the sample CP (CZTS precursor). Upon 1 min annealing, the columnar structure of the CZTS film was converted into a dense packing of fine grains. Extending annealing to above 5 min, larger CZTS grains were grown accompanied by obvious appearance of ZnS crystals (bright crystal in SEM image). Furthermore, the SnS phase with the noticeable plate structure can be found on both CZTS surface and rear after 13 min annealing, similar to our previous report.²⁵ The morphological change and observed phases in Figure 2 are in good agreement with XRD results in Figure 4a and 4b. A further analysis of the grain growth in the CZTS films is displayed in Figure 3a. In the simplified model for an equiaxed grain growth, the grain size R is proportional to the dwell time t at a constant annealing temperature (R is proportional to $t^{1/n}$, where $n=2$ for an ideal grain growth, and $n>2$ for a slow grain growth hindered by

precipitates).²⁶ This assumes that the grown grain is much larger than the initial grain/nuclei at the given temperature. It holds true for our case, since the width of the columnar structure of the sample C0 (Figure 2b) is still much smaller than the film thickness, and thereby the potential size of the CZTS nuclei core is considered negligible. As shown in the inset of Figure 3a, the fit for n is between 2.2–2.4 and the spread of the grain size becomes significant for longer annealing time.

Figure 2. SEM cross-section of the CZTS films with different annealing time

Figure 3b shows the plot of CZTS compositions of all samples, derived from EDS measurements that were made on areas of CZTS grains free of apparent secondary phases. It is found that Zn content in the CZTS phase tends to decrease (while still higher than 25%) much more than the Sn-content, especially for annealing beyond 5 min, ultimately causing the composition of CZTS films to approach stoichiometry and to lose their Cu-poor character. The significant reduction of Zn content in CZTS must come from the precipitation of ZnS secondary phases outside the CZTS grains, since we do not observe changes in the integral composition of the CZTS films via XRF. One consequence of the appearance of secondary phases is a change in the stoichiometry of the CZTS phase over time, likely alternating its defect chemistry at the same time. This important remark is discussed in detail later.

Time resolved P_{S_2} dependence formation of secondary phases in CZTS. Figure 4a and 4b show the XRD patterns of the CZTS films with Bragg-Brentano and grazing incidence configurations. It can be seen that GIXRD (Figure 4b) reveals more features of CP. Most notable is a broad peak at 51.8° that can be assigned to the highly disordered wurzite structure,²⁷ with the most intense $\Sigma 112$ peak at 28.4° that is also seen with Bragg-Brentano XRD.

Figure 3. (a) Relationship between annealing time and the full width at half maximum (FWHM) extracted from near resonant Raman with 785 nm excitation laser wavelength. The inset shows the grain size (measured from the top view SEM configuration (Figure S3)) as a function of annealing time. (b) Plot of the EDS composition of the annealed CZTS film; the black color represents the precursor, and the graded color represents the sample prepared with different annealing time. The CZTS single-phase region, with nearly stoichiometric composition, is marked by the red open circle for eye guidance. The gray solid line marks the tie line of different defect complex.

There are two additional peaks next to $\Sigma 112$ peak, which we cannot assign confidently, and we speculate they could be features of our metastable Cu-Zn-Sn-S precursor film. Upon annealing, the recrystallization process was initiated in the precursor film, and a tetragonal structure started to form (peaks at 44.9° , 47.3° and 56.2° in Figure 4b). Above 1 min annealing, polycrystalline tetragonal-CZTS was fully formed, with the emerged peaks at 23.1° (110), 29.7° (103) and 37.9° (211).

In Figure 4a and 4b, along with the emergence of the CZTS phase, we also observed that there was a gradual change of the Sn-S secondary phases. SnS_2 (XRD peak at 15°) appeared at the start of the annealing process (C0), and persisted until the annealing was extended to 3 min (samples C1, C2 and C3). After 5 min annealing (C5), the SnS_2 phase was gone while the SnS phase (peak at 31.8°) appeared in samples C13 and C40. In addition, to confirm the distribution of Sn-S phases, we performed Raman with 532 nm excitation laser wavelength on both surface and rear (we used a lifted off technique to remove CZTS film from the CZTS/Mo S_x interface) of all CZTS films, and found that Sn-S phases appeared on both sides with a similar evolution to that of XRD. These phases cannot be observed in bulk CZTS based on SEM cross-section mapping (not shown here).

We further performed Raman with a 325 nm laser wavelength (UV-Raman) on both surface and rear of CZTS films to investigate the ZnS secondary phase, since UV-Raman facilitates a resonant enhance effect on ZnS,²⁸ which is powerful to distinguish CZTS and ZnS phases.²⁹ As shown in Figure 4c, we observed that the ZnS phase appeared faster on the rear than at the surface of the CZTS films. With a more detailed summary of UV-Raman in Figure 4d, we can identify that both SnS_2 and ZnS appeared on the CZTS rear with the SnS_2 phase but not the ZnS phase being already formed for C0. This implies that the annealed CZTS

film must prefer a Zn-rich composition since the overall composition of the CZTS film always remained unchanged. Another important UV-Raman observation regarding the ZnS secondary phase is that the LO1/LO2 peak ratio decreases with increased annealing time (the inset of Figure 4c). The LO1/LO2 value was reported to be significantly increased, resulting from the quantum confinement effect, for ZnS nanoparticles of few nanometer size,²⁸ whereas LO1/LO2 became low and saturated when the ZnS crystal size was above 30 nm. In our case, we observed a similar trend, that this peak ratio (both CZTS surface and rear) was apparently reduced and nearly saturated after 2 min annealing time.

Furthermore, we also excluded other secondary phases that could possibly exist in our CZTS films by using Raman measurements with multiple laser wavelengths on CZTS surface and rear (see Figure S3), such as Cu_3SnS_4 ³⁰ (785 nm laser wavelength), Cu_2SnS_3 ¹⁸ (532 nm laser wavelength). The results of Raman and XRD lead us to conclude that only ZnS and Sn-S compounds coexist with the CZTS phase in our annealed films.

Interestingly, the evolution of Sn-S secondary phases in CZTS films has a similar trend to that of the annealed SnS_2 films in Figure 1, i.e. SnS_2 gradually converted to SnS over time. However, it needs to be remarked that C5 is exceptional because a weak Raman signal of Sn_2S_3 , which is invisible in XRD (likely due to its small amounts), can only be seen on the CZTS rear (Figure S4). Since the P_{S_2} reduction is the key to the Sn-S phase transformation (Figure 1), we propose the possible explanation for formation of Sn-S secondary phases as follows. Formation of SnS_2 in CZTS must originate from the composition effect, since the initial composition of the precursor is slightly Sn-rich (Cu/Sn-1.9) and the experiments were carried out with Sn-S free environment. Upon 5 min anneal, the already decreased P_{S_2} reduces SnS_2 to SnS on the CZTS

Figure 4. (a) Bragg Brentano XRD and (b) XRD at 1° grazing incidence angle of the CZTS films with different annealing time; (c) Summary of the 2nd order peak of ZnS and CZTS from UV Raman (the rectangular represents the phase margin), and there is no ZnS measureable on the CZTS rear for the sample C0. There are two peaks showing up for the sample C2, which belongs to CZTS and ZnS respectively. The inset shows the peak height ratio of 1st order (LO1) and 2nd order (LO2) of the ZnS phase as a function of the annealing time. (d) Contour plot of the UV Raman of the evolution of secondary phases on the rear of the annealed CZTS as annealing advances, each individual Raman spectrum is normalized.

surface while the volatile SnS is then quickly vaporized due to the unsaturated SnS vapor (no observation of condensed SnS phase after annealing process) in the annealing atmosphere. The process occurring on C5 must be accompanied by a rapid loss rate of P_{S_2} , which agrees with the observations on S5 in Figure 1. The observed Sn_2S_3 on CZTS rear also indicates that the influence of P_{S_2} is stronger on CZTS surface. In the end, for C13 and C40 the insufficient P_{S_2} caused the CZTS surface to decompose. The significantly segregated SnS in CZTS after thermal process could result from the decomposition of CZTS surface and the SnS_2 secondary phase as well as partly from the SnS_2 monitoring material.

Formation of ZnS is a result of a diffusion process when the concentration of this phase is beyond its solubility limit in CZTS, or when the critical nucleation energy of ZnS is reached. The nucleation energy could be perturbed by the stress or the surface energy of a film, which could be a reason for the faster formation of the ZnS particles on CZTS rear because of the possible difference in the thermal expansion of Mo and CZTS layers during the annealing

process. The stress introduced at the interface of Mo/CZTS could accelerate the formation of bulk type ZnS phase, which explains the early saturation of LO1/LO2 peak (the inset of Figure 4c). On the CZTS surface, the formation of ZnS can be apparently affected by P_{S_2} . There is a higher chance for ZnS formation and growth when CZTS surface is decomposed, as we can see ZnS crystals of about 100 nm size in SEM images in Figure 2 and Figure S2. The precipitation of ZnS could prohibit CZTS grain boundary migration, resulting in non-uniform CZTS grain growth (the inset of Figure 3a). The ZnS grains could also be coarsened when they are connected, as was shown in SEM images (Figure 2 and Figure S2).

In summary, as the annealing process advances, the development of Sn-S phases in CZTS is strongly influenced by P_{S_2} , while the evolution of the ZnS phase is dominated by diffusion process with a possible enhancement of the effect from P_{S_2} . The formation of secondary phases as a function of annealing time is summarized in Table 2.

Table 2. Summary of secondary phases and anticipated defects in different CZTS film

Anneal. Time (min)	Sample	Secondary phase in CZTS film		Anticipated contributing defects
		Surface	Backside	
0	C0	SnS ₂	SnS ₂	A+B, Cu/Zn cation disorder
1	C1	SnS ₂	ZnS, SnS ₂	A+B, Cu/Zn cation disorder
2	C2	ZnS, SnS ₂	ZnS, SnS ₂	A+B, Cu/Zn cation disorder
3	C3	ZnS, SnS ₂	ZnS, SnS ₂	A+B, Cu/Zn cation disorder
5	C5	ZnS	ZnS, Sn ₂ S ₃	A+B, Cu/Zn cation disorder
13	C13	ZnS, SnS	ZnS, SnS	B, Cu/Zn cation disorder
40	C40	ZnS, SnS	ZnS, SnS	B, Cu/Zn cation disorder

Time resolved P_{S2} dependence on defect formation in CZTS. Studying the secondary phase segregation provides valuable information to infer the possible structural defects in the CZTS bulk. For example, the aggregated defects of 2Zn_{Cu}+Zn_{Sn} can lead to small ZnS-like domains.³¹ This is relevant because the type of dominant defects can influence core properties of CZTS such as the band gap and doping. In Figure 3a, we also observe an increased FWHM of CZTS peak at 338 cm⁻¹ in the NR-Raman with longer annealing. An increased FWHM of this peak could originate from decreased correlation length³² due to structural defects in CZTS, such as defect complexes and clusters (as indicated in Figure 3b).

Among all type of defects or defect complexes in CZTS, the Cu/Zn cation disorder (Cu_{Zn}+Zn_{Cu} defect pair) is considered as the most plausible complex, due to the similarity of the Cu⁺ and Zn²⁺ cation size and its low formation energy.³³⁻³⁴ The concentration of this defect pair causes changes to peak intensity ratios in the NR-Raman. As indicated in Figure 5a, the Q and Q' parameters can be linked to the degree of Cu/Zn cation disorder and be correlated to the type of defect clusters (in the latter case, only for material with high Cu/Zn ordering).^{31, 35} The definition of Q and Q' can be seen in Figure 5a. We performed an additional slow cooling process³⁵ to enhance Cu/Zn ordering and allow investigation of the dominant defect complexes as function of annealing time. As presented in Figure 5a, reduction in Cu-Zn disorder drastically improves the overall structural quality of CZTS film, since the main Raman A modes (287 cm⁻¹ and 338 cm⁻¹) are sharpened with relatively reduced background intensity (from 250 cm⁻¹ to 375 cm⁻¹).

Figure 5b shows that the RT-PL red shifts over annealing time. The plot in Figure 5c and 5d shows the correlation between the ordering parameters from NR-Raman and the RT-PL energy. Before ordering, a linear relationship between RT-PL energy and ordering parameter can be seen in Figure 5d. Upon ordering, we find that the defect evolution in CZTS becomes evident and involves three stages, see Figure 5c: I) short annealing time, intermediate Q(Q') and high RT-PL energy; II) Intermediate annealing time, high Q(Q') and intermediate RT-PL energy; and III) Long annealing time, low Q(Q') and low RT-PL energy. Such results demonstrate that complex defect interactions beyond

Cu/Zn disorder evolve in CZTS over annealing time, since RT-PL energy does not increase monotonically with increased Q(Q') as shown in a recent report.³⁶

Figure 5. (a) Typical Raman scattering with 532 nm and 785 nm laser wavelength on the annealed CZTS film before/after ordering treatment, and the definition of order parameters Q and Q' calculated from different peak intensity ratios. (b) The correlation between room temperature photoluminescence (RT-PL) peak position and annealing time; The RT-PL peak position is corrected from the interference effect (see Figure S5).³⁷ (c) The ordering parameters defined by NR-Raman peak height ratio as function of RT-PL peak position (c) after the ordering treatment; (d) as annealed CZTS (before ordering treatment). The number next to each plot indicates the corresponding annealing time, as seen in figure (b). The (open/solid) stars in all figures are the samples (C1R and C13R) annealed without SnS₂ film, in order to verify the potential influence of SnS₂ film on CZTS thin film during the annealing process.

As revealed in Figure 1e, we understand that P_{S_2} varies strongly over time in the non-equilibrium annealing process. The primary question raised now, for Figure 5c and 5d, is which variable dominates the quality of the CZTS film. In the following, we will take a closer look at the possible causes behind the three stages in Figure 5c.

We firstly observed in Figure 5c that the overall trend of change in Q and Q' is similar for all three stages, in particular for the first two stages where the value of Q and Q' is above 3. This suggests that the defect in CZTS at shorter annealing time may be abundant in A-type defect. It has been reported by Paris et al. that a high Q (>4) accompanied by a high Q' (>3) can be attributed to A-type related CZTS.³¹

In stage I (1-2 min annealing), the atomic diffusion process is dominant in CZTS film because of a constant high P_{S_2} according to Figure 1. Since the CZTS phase at this stage is Zn-rich, and the CZTS composition lies in the A+B type defect regime in Figure 3b, these defect pairs are considered abundant in CZTS. In the B-type defect, two Cu and one Sn atoms will be replaced by three Zn atoms, suggesting that i) the Cu/Zn cation ordering may be spatially clustered due to the high barrier for diffusion³⁵; ii) a fraction of the Zn atoms in the CZTS lattice perhaps locally shift to ZnS-like coordination, forming potential nucleation sites for ZnS. The high LO1/LO2 ratio in the inset of Figure 4c is a good indication that the "ZnS" may be in nanometer scale spatially. For C2, atomic diffusion tends to aggregate Zn-rich areas into ZnS nuclei (LO1/LO2 decreases with a large spread from surface and rear in the inset of Figure 4c). Because $Q(Q')$ is nearly constant in this stage, the RT-PL shift can be related to a change in the net effect of the hybrid defect (clusters). As was reported by the DFT calculations,^{36, 38} one Cu/Zn antisite pair within 4 unit cells can reduce the effective bandgap by about 100-200 meV. Besides, bandgap narrowing effects from A-type as well as B-type defects are supposed to be slightly lower than Cu/Zn cation disorder on the valence band edge.³³ Thus, we speculate the gradual reduction of B-type defect in interaction with Cu/Zn disorder and A-type defects could be a reason for the RT-PL red shift.

In stage II (3-5 min annealing), the diffusion process in CZTS starts to be influenced by the drop of P_{S_2} , as indicated in Figure 1e. The steadily reduced P_{S_2} means that CZTS could start losing S or start decomposing. Simultaneously, the value of LO1/LO2 in the inset of Figure 4c becomes almost consistent on both the surface and rear of the CZTS film, which suggests that ZnS grains could be separated from CZTS. The separated ZnS from CZTS may reduce the concentration of Zn rich defects in CZTS lattice, leading to a high $Q(Q')$ value (e.g. due to a decrease in B-type defect). Nevertheless, other influences from vacancies (S or Cu) as well as atomic diffusions are hard to predict, since the reduction of P_{S_2} is rapid in this regime (see Figure 1d). Even though the B-type defect could be reduced structurally, the perturbation of other factors, e.g. the concentration of the S vacancy, may also be dominant by affecting the concentration of other type of defect.³⁹ Therefore, we observe high $Q(Q')$ but nearly pinned RT-PL energy in this region.

In stage III (above 5 min annealing), the diffusion process can be greatly influenced by a decrease in P_{S_2} , since the low P_{S_2} can continuously trigger CZTS decomposition (Reaction 1 in Table 1). The composition of the CZTS phase is altered towards less Zn-rich because of ZnS segregation (see compositional plot in Figure 3b), resulting in a possible change of dominant defect in the CZTS from (A+B)- to nearly pure B-type. The linear behavior of RT-PL energy and ordering parameters in this region matches well with previous experimental studies on nearly B-type CZTS.³⁵⁻³⁶ In this region, there is limited Cu/Zn cation ordering owing to the high activation energy barrier for ordering in B-type CZTS,³⁵ which is considered to cause large bandgap fluctuations. We must emphasize that $Q(Q')$ values in regions I and II may not necessarily be comparable to those in region III, since it is possible that $Q(Q')$ is also affected by the concentration of the different defect complexes (A or -B-type), not just by Cu/Zn disorder.

Turning to the non-ordered CZTS in Figure 5d, we note that the RT-PL peak position follows the $Q(Q')$ value linearly, similar to stage III in Figure 5c. This is again anticipated, because of the very limited Cu/Zn ordering resulting from the fast cooling process.³⁵ Most importantly, here we also show that a combined effect from P_{S_2} evolution, in addition to diffusion process, can greatly influence the ordering parameters as well as RT-PL energy, by means of changing the defect types. The high quality of CZTS, including a RT-PL peak of 1.39 eV and a low FWHM of Raman A mode peak (Table S1), can be prepared within 1 min anneal that provides sufficient P_{S_2} . The CZTS quality can be further improved by using an optimized 35 h cooling process, and the obtained RT-PL of 1.43 eV is significantly higher than commonly reported RT-PL value of 1.25-1.32 eV of CZTS in literature.⁴⁰⁻⁴¹

Lastly, to inspect any impact of the monitoring material (SnS_2 film) on the CZTS film under the same annealing batch, two reference samples with the same annealing condition but without loading SnS_2 film were prepared, as indicated by the stars in Figure 5b-d. As expected, the SnS_2 film has a larger impact on the decomposing than the intact CZTS. Under deficient P_{S_2} , the decomposed SnS_2 film can restrain the CZTS surface decomposition by saturating the box with SnS vapor. In contrast, the effect from the presence of the SnS_2 monitoring film on CZTS is negligible under sufficiently high P_{S_2} .

In short, we find that as the P_{S_2} reduces over annealing time, the defect construction in CZTS seems to alter simultaneously. It can be concluded that in the ordered case, the bandgap shift seen in RT-PL is dominated by the type of defects in CZTS, which can be affected by P_{S_2} (particularly from (A+B) to B type). In the non-ordered case, Cu-Zn disorder dominates the RT-PL peak shift. The development of the possible defects in CZTS over time is summarized in Table 2.

Figure 6. (a) Current-voltage characteristics and (b) External quantum efficiency (solid line) and the RT-PL spectra (dash line) of the CZTS solar cells; (D1) 1 min anneal, loading SnS_2 ; (D13R) 13 min anneal, no loading SnS_2 ; (D40) 40 min anneal, loading SnS_2 ; All devices were fabricated from CZTS absorbers without additional ordering processes. All RT-PL spectra were corrected by considering the interference effects.³⁷ Respective solar cell parameters can be found in Table 3.

Table 3. Device performance with the CZTS film prepared from different annealing time

Device	Anneal. time (min)	P_{S_2}	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	RT-PL (eV)	E_{g, EQE^2} (eV)	V_{oc}^{def} (V)
D1	1	Sufficient high	711	13.8	62.7	6.2	1.39	1.56	0.85
D13R	13	Insufficient (Ref.)	566	16.6	56.8	5.3	1.32	1.49	0.92
D40	40	Insufficient	301	13.0	51.4	2.0	1.29	1.43	1.13

* J_{sc} is calculated based on 0.5 cm² total area; V_{oc}^{def} is defined by $E_{g, EQE^2}/q - V_{oc}$, where q is the elemental charge

Photovoltaic device performance. Given high RT-PL energy resulting from the CZTS prepared under sufficient P_{S_2} , it is presumed the open circuit voltage (V_{oc}) of the solar cell devices could also be high. To verify this hypothesis, we fabricated CZTS solar cells from extreme regimes of the anneal process, namely D1 (1 min, high P_{S_2}), D40 (40 min, low P_{S_2}) and D13R (13 min, Ref). The device characteristics are displayed in Figure 6. As anticipated, V_{oc} of D1 is indeed improved, above 700 mV (700–730 mV over 30 cells with several repeated experiments), compared to our reference device D13R (usually about 600mV¹⁹). The high V_{oc} of D1 is independent of the presence of SnS_2 loaded together with CZTS during the anneal, proving that the SnS_2 monitoring film does not have impact on CZTS when there is sufficient P_{S_2} .

The improvement of V_{oc} is in good agreement with the increase of the RT-PL energy and bandgap of CZTS absorber (see Figure 6b). As summarized in Table 3, the derived E_g values from the QE edge in Figure 6b are 1.56 eV, 1.49 eV and 1.43 eV for D1, D13R and D40, respectively. This red shift of E_{g, EQE^2} from D1 to D40 is consistent with the RT-PL results in Figure 6b and Table 3, indicating that there could be an increase in the bandgap energy of CZTS (or a decrease in the bandgap narrowing) when P_{S_2} can be preserved sufficiently. Even though the shift tendency of RT-PL and E_{g, EQE^2} is similar, we find that the difference between these two values is almost unchanged (~150 mV). This could stem from the Cu/Zn disorder (see Figure 5d) that is influenced by P_{S_2} during annealing. As was reported recently for CZTSe solar cells, intentionally reducing

Cu/Zn disorder in the CZTSe film can lead to the enhancement of V_{oc} as well as the same amount of blue shift of RT-PL and optical bandgap, which matches well with our findings here.⁴²

Furthermore, it is noticeable in our work that the greater V_{oc} of D1 is accompanied by a reduced V_{oc} deficit (see Table 3), which could suggest that the different defect chemistry resulting from high P_{S_2} during annealing of the CZTS indeed may substantially have an impact on the solar cell. However, we also observe that the short circuit current (J_{sc}) of the device D1 is lower than the reference D13R. The reason for a low J_{sc} of device D1 remains open, and we will investigate the electrical behavior of these solar cells in future work. However, increased bandgap of D1 can be one explanation for the reduced J_{sc} .

The result of the solar cell performance in this work is very interesting. It clearly points to the fact that the defect in CZTS can be effectively modified under a precise monitoring of the P_{S_2} . Moreover, we can further boost the V_{oc} by an additional ordering treatment on the annealed CZTS film before our standard chemical bath deposited CdS deposition, and the demonstrated device shows promising performance (the champion device fabricated with the ordering treatment has V_{oc} of 783 mV, J_{sc} of 14.1 mA/cm², FF of 63.2% and PCE of 7.1%). We believe that by facilitating the front interface of the CZTS with alternative buffer layers,⁴³⁻⁴⁴ there is strong potential for further improvement of the solar cell efficiency.

Conclusion

We showed a powerful method to achieve quasi-in-situ monitoring of P_{S_2} for multinary compound synthesis during high temperature processing. The effective P_{S_2} directly involved in the material synthesis can be estimated by investigating the phase transformation of an analogous binary compound. To verify this idea, we used Sn-S phase transformation to monitor the P_{S_2} . It was found that P_{S_2} has considerable dynamic feature underlying the annealing time during the thermal process. Furthermore, we successfully correlated this reduction of P_{S_2} over time to the gradual modification of the CZTS properties in the same non-equilibrium annealing process, which includes secondary phase formation and defect evolution in CZTS. Eventually, it was demonstrated that sufficiently high P_{S_2} for the CZTS synthesis can improve the V_{oc} of solar cell devices above 700mV. The key issue tackled in this work, i.e. monitoring chalcogen partial pressure, creates scope for deeper understanding of the relationships between material synthesis and properties.

ASSOCIATED CONTENT

Supporting Information. Additional tables including specific parameters of Raman results as well as figures of Raman spectra, SEM images and RT-PL spectra

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