Practical limitations to selenium annealing of compound co-sputtered $\text{Cu}_2\text{ZnSnS}_4$ as a route to achieving sulfur-selenium graded solar cell absorbers

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Abstract

The suitability of selenium annealing as a technique to introduce energy band gap gradients via sulfur-selenium substitution in $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) films is evaluated. Compound co-sputtered CZTS precursors are annealed in selenium atmosphere at 425°C, either as-deposited or after a short time sulfur pre-anneal. The films are investigated by Raman spectroscopy and X-ray diffractometry, and the spatial distribution of elemental species measured by secondary ion mass spectrometry and energy dispersive X-ray spectroscopy. Sulfur-selenium gradients are not achieved for the as-deposited precursor. Sulfur-selenium gradients are achieved in the early stages of annealing for pre-anneal samples, where $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) formation is found to be correlated spatially with sodium distribution. These gradients are lost as the annealing progresses. Selenisation occurs by CZTSSe grain growth, rather than by direct substitution of selenium for sulfur. The spatial correlation of high sodium concentration with CZTSSe formation suggests that liquid-phase sodium selenide facilitates selenium incorporation during recrystallisation, limiting the practicality of anion-grading of CZTSSe during the annealing step as a means of establishing a graded band gap.

Keywords: CZTSSe, diffusion, crystallisation, sodium, band gap gradient.

1. Introduction

The copper-zinc-tin-sulfide/selenide quaternary semiconductor material (hereafter CZTSSe or CZTS for the pure sulfide) is seen as a potential replacement for the mature copper-indium-gallium-selenide (CIGS) system as the absorber material in thin film solar cells. Although its record device sunlight-to-power efficiency remains 12.6% [1], CZTS absorbers are composed of earth-abundant materials, and show promise for future solar cell applications and as model systems for the improvement of other technologies. High efficiency CIGS solar cells employ In-Ga gradients through the thickness of the absorber film to modify the band gap and minimise recombination [2]. It is reasonable to expect the necessity of such band gap engineering in

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CZTSSe devices as one of the steps to improve efficiencies to compete with existing market technologies. It is also necessary to study how the peculiarities of the quaternary system such as band misalignment [3], deep defects within the absorber [4], band gap fluctuations from cation disorder defects [5], secondary-phases [6], and back-contact issues [7] might affect the efficacy of and fabrication steps necessary for such a band gap grading. This provides motivation for studies into band gap grading in CZTSSe.

The band gap of pure selenide CZTSe is 0.96 eV, and for the pure sulfide CZTS, 1.5 eV [8]. Substitution of one chalcogen for the other scales the band gap in an approximately linear fashion, with the majority of the change in the conduction band [9]. Increasing the sulfur proportion of the anion towards the front could result in a wider front band gap—a ‘front grading’. Increasing the selenium proportion from low Se content towards the back to high Se content towards the front could yield a wider back band gap—a ‘back grading’. A front S-Se grading was recently reported for CZTSSe from a stacked metallic precursor and the use of SeS_2 as the chalcogen source [10], but the mechanism of the gradient formation was not fully investigated. Back Se-S gradings have been reported for sequentially deposited compound-sputtered and metallic precursors [11], where it was noted that Se incorporation was less inhibited for stacked precursors than for CZTS films. A back grading has also been reported from solvent-based ink precursors sequentially annealed in sulfur then selenium [12], with preferential selenisation at the surface exposed directly to the selenium gas phase postulated as the mechanism responsible for the reported back grading. Good device properties were also reported for a CZTSSe sub-module and attributed to a back grading [13], but the mechanism of gradient formation was not made clear.

It is also known that diffusion of selenium in CZTSe is rapid [14], and that for nanoparticle precursors CZTSSe crystallisation is dependent on nucleation and growth processes rather than surface-down reaction of the existing precursor with the gas phase [15]. We have also reported that for recrystallised CZTS films, selenisation results in rapid diffusion of selenium via grain boundaries, and that growth is limited by processes other than selenium diffusion through the film, resulting in phase segregation between the CZTS sulfide and the CZTSSe selenide [16]. These studies call into question how annealing in selenium atmosphere has been sufficient to establish simple front-back chalcogen gradients in CZTSSe, and how such processes might be controlled. Fine control over material grading is important for the analogous CIGS system, especially in the case of front band gap grading [2, 17]. Modelling of CZTSSe systems indicates sensitivity to the type, position, and extent of band gap grading [18].

Control of a simple ‘back graded’ band gap in CZTSSe must require fine control of both the recrystallisation of the absorber and the chalcogen distribution within that absorber. The selenium-to-sulfur gradient must exist within single grains in a continuous manner to have a device-positive impact on collection and recombination. The mechanisms governing chalcogen substitution and crystal growth must therefore be understood in order to design and improve processes to form such chalcogen gradients. In this study, we study progressive selenisation of CZTSSe starting from compound sputtered precursors in which SnS, ZnS, and CuS are co-sputtered rather than sequentially layered. In doing so we hope to minimise cation-specific effects

such as differing chalcogen affinities, chalcogen diffusion coefficients, or sequential crystallisation through non-CZTS intermediates such as CuSn_2Se_3 . We also investigate the effect of sulfur pre-annealing prior to selenisation, in order to determine if there is some ‘middle state’ of CZTS formation which restricts selenisation sufficiently to form a chalcogen gradient without significant sulfide / selenide phase segregation.

2. Experimental Details

Bilayer molybdenum back contacts were sputtered onto soda-lime glass substrates. $\text{Cu}_2\text{ZnSnS}_4$ precursor material was co-sputtered using a Lesker CMS-18 sputter system, in a 666 Pa argon atmosphere from sulfur-compound targets CuS, SnS, and ZnS. CuS and SnS were DC-sputtered at power densities 1.54 W cm^{-2} and 0.66 W cm^{-2} , respectively, and ZnS RF-sputtered at 3.3 W cm^{-2} . Three separate sets of $2.5 \text{ cm} \times 2.5 \text{ cm}$ precursors were fabricated, all with slightly different cation ratios. Elemental compositions for the three precursor families were determined by Rutherford back scattering-calibrated X-ray fluorescence measurements. These compositions are listed in Table 1 along with the other experimental conditions. Some changes in experimental conditions within each series are printed in colour for ease of reading.

Film	Cation conc. ratio		Time [min.]	
	$\frac{[\text{Cu}]}{[\text{Sn}]}$	$\frac{[\text{Zn}]}{[\text{Cu}]+[\text{Sn}]}$	S	Se
P	1.88	0.34	-	-
PSe10	1.88	0.34	-	10
S	1.88	0.34	5	-
SSe10	1.88	0.34	5	10
2SSe10	1.90	0.33	10	10
2SSe20	1.90	0.33	10	20
2SSe30	1.90	0.35	10	30
2SSe45	1.90	0.35	10	45

Table 1: Table of sample cation concentration ratios and sulfur (S, 500°C) and selenium (Se, 425°C) annealing conditions. Important differences in experimental conditions are marked with bold font.

For the annealing, precursors were either selenised directly or underwent a sulfur anneal prior to selenisation. Annealing was performed in a pyrolytic carbon coated graphite box. Sulfur annealing was performed with 40 mg of elemental sulfur, at 500°C and an argon pressure of $4.66 \times 10^4 \text{ Pa}$. Both the sulfur-annealed films and precursors were selenised with elemental selenium at 425°C , to promote slow incorporation of selenium into the absorbers. Selenisations were performed for various times at an argon pressure of $3.53 \times 10^4 \text{ Pa}$, using 40 mg of elemental selenium. The untreated precursor is denoted sample ‘P’. After selenisation for 10 minutes, the suffix ‘Se10’ is added, so that sample is called ‘PSe10’. Five minute sulfur annealed samples were ‘S’ and its subsequent 10 minute selenisation ‘SSe10’. Ten minute sulfur annealed samples were selenised for 10, 20, 30, and 45 minutes. These samples are prefixed ‘2S’ to indicate their longer sulfurisation, and have suffixes ‘Se’ which show their selenisation times: the samples are ‘2SSe10’, ‘2SSe20’, ‘2SSe30’, and ‘2SSe45’. The list of samples with their preparation conditions is given in Table 1.

Grazing incidence X-ray diffraction (GIXRD) characterisation was performed in a Siemens D5000 diffractometer. Raman spectroscopy was performed using a Renshaw Invia equipped with 532 nm laser. Raman measurement of the back side of samples was achieved via a destructive lift off procedure. Films were glued top-down to a slide of clean glass and allowed to dry. Once adhesion was complete, the film substrate was removed by force, leaving a fragment of the film on the glass, cleaved along the interface between the film and the Molybdenum back contact. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) linescans were obtained using a Zeiss Leo 1550 with a 5kV accelerating voltage. Low voltage was used to minimise the interaction volume and improve the spatial resolution of the EDX. Lines analysed were Cu-L, S-K, Se-L, Zn-L and Sn-L. Cu-L and Zn-L overlap but were deconvolved using Oxford Instruments' AZtec software. Sn-L had a low signal-to-noise. Cation lines could be resolved to the extent that measured cation elemental ratios were as expected. The Mo-L line overlaps the S-K line heavily and was not deconvolved: the back Mo contact of the film can be identified by the sudden rise in the S signal. Secondary ion mass spectrometry (SIMS) depth profile measurements were performed using a Cameca IMS 7f instrument with a primary beam of 5 keV Cs⁺ ions. The beam was scanned across a raster of 200 x 200 μm and an analyzed area with a diameter of 62 μm . In order to minimize the potential matrix effects due to a change in $[S] / ([S] + [Se])$ ratio, MCs⁺ clusters were detected in SIMS.

3. Results

A survey of sulfur anneal conditions was performed to find a state between the CZTS precursor and large-grain CZTS for which subsequent selenisation might produce either chalcogen gradients or variations in the profile of selenisation to facilitate further investigation. Even at the relatively low temperature of 500°C, large CZTS grains crystallised after 20 minutes or more, and produced sulfide/selenide grain segregation on selenisation. However, films sulfur-annealed at 500°C for less than 20 minutes remained morphologically similar to precursors, and selenised differently to both large grain CZTS and un-sulfurised precursor samples.

In the first instance, the effects of a 10 minute 425°C selenisation on both precursor (sample 'P') and 5-minute, 500°C sulfur annealed (sample 'S') films were investigated. In the cross-sectional SEM images shown in Fig. 1, the morphology of the sulfur pre-annealed 'S' is very similar to the untreated precursor 'P'. The main observable difference is the presence of large surface structures on 'S', identified later by GIXRD as SnS₂. A 425°C selenium anneal produced samples PSe10 from the precursor 'P' and 'SSe10' from the sulfur-annealed 'S'. The morphology within the absorbers is very similar between the selenised samples, with one subtle exception: crystallisation very close to the back contact is significantly more advanced in the sulfur-annealed sample, SSe10. The structure at the back contact is more smooth and laterally continuous than in PSe10.

Secondary ion mass spectrometry was used for elemental analysis in depth. MCs⁺ SIMS profiles are shown in Fig. 2 for samples 'P', 'S', PSe10, and SSe10. For selenised precursor PSe10, selenium is spread throughout the CZTSSe, with a slight selenium gradient from the front surface, but no complementary

(a, P)

(b, S)

(c, PSe10)

(d, SSe10)

Figure 1: Cross-sectional SEM images for samples (a) P; (b) PSe10; (c) S; (d) SSe10. Samples 'P' and 'S' have very similar morphology, but recrystallisation at the back contact in SSe10 is more advanced than in PSe10.

sulfur gradient. Sulfur- and selenium-annealed SSe10 shows an increase in selenium immediately at the back contact, tapering off several hundred nanometres into the film. This selenium extends further into the film than the back contact MoSe_2 peak of PSe10, and indicates the formation of a CZTSSe selenide near the back contact. These data match the higher degree of back contact crystallisation seen by SEM.

The ^{23}Na distributions in the SIMS data in Fig. 2 are of interest. Due to the possibility of $^{78}\text{Se}^{78}\text{Se}$ interference with the $^{23}\text{Na}^{133}\text{Cs}$ signal, these profiles were verified with O_2+ SIMS. The precursor ‘P’ has a very low level of sodium: either there is no sodium present, or a very small amount distributed through the film. Following 10 minute selenisation in PSe10, a higher amount of sodium is distributed evenly through the film, with a small accumulation at the front and back of the CZTSSe layer. In contrast, the sodium distribution in ‘S’ has been changed dramatically by the sulfur pre-anneal: there is an accumulation of sodium in the first several hundred nanometres at the back of the film, as well as an accumulation near the front surface of the film. Selenisation spreads this sodium gradient out in SSe10 while simultaneously segregating the selenium in a pattern that correlates well with the preceding sodium distribution: the selenide crystallises more completely near the back contact.

The pre-annealed film underwent more complete selenide crystallisation towards the back contact than the precursor. A longer sulfurisation of 10 minutes was used to attempt to increase the back-contact effect without crystallising large grains in the sulfur anneal. Selenisations were performed for 10, 20, 30, and 45 minutes: samples 2SSe10, 2SSe20, 2SSe30, and 2SSe45, respectively. EDX was used to probe the uniformity of the selenisation for all samples, but for brevity only the EDX line scans for samples 2SSe10-45 are shown in Fig. 3. The EDX profiles for the other samples reproduced similar details as the SIMS data reported in Fig. 2, but showed a uniform selenium distribution in the CZTSSe layer for PSe10. The EDX profile of the 10 minute selenised film 2SSe10 reveals the familiar preferential selenisation towards the back contact. With increasing selenisation time, more selenium is incorporated towards the front of the film. As selenisation time increases to 30 minutes (2SSe30) and 45 minutes (2SSe45), the selenium distribution becomes less uniform, with some locations showing the kind of initially desired back-to-front selenium grading as in Fig. 3(c), and others showing sulfide and selenide grain segregation as in Fig 3(d). EDX density maps (not included) confirmed that at 30 minutes of selenium anneal and beyond, the lateral uniformity of the selenium distribution is compromised, and distinct sulfide- and selenide-rich grains are formed. From a previous study [16], it is known that continuing to selenise such structures results in the growth of the selenide grains via removal of cations from the sulfide grains, so longer selenisations were not attempted.

Raman spectra were recorded for both the front-side and back-side after lift-off of the CZTS/CZTSSe layers, and are shown in Fig. 4. $\text{Sn}(\text{S},\text{Se})_2$ surface structures were excluded from the beam spot if possible. Front side SnSe_2 structures were too small to avoid for sample PSe10. In the precursor ‘P’, the CZTS peak at 338 cm^{-1} [19] is present, and there is no CZTSe peak. For the back side Raman measurements, all selenised samples show a CZTSSe peak between the CZTSe position at $\sim 197\text{ cm}^{-1}$ [11] and the CZTS peak. For the front side measurements, there is no CZTSSe detected for sample SSe10, and only a small peak for

(a, P)

(b, PSe10)

(c, S)

(d, SSe10)

Figure 2: MCs^+ SIMS profiles for samples (a) P; (b) PSe10; (c) S; (d) SSe10.

(a, 2SSe10)

(b, 2SSe20)

(c, 2SSe30)

(d, 2SSe45)

Figure 3: Surface-to-back contact EDX line scans for (a) 2SSe10, (b) 2SSe20, (c) 2SSe30, and (d) 2SSe45, showing that the initial back contact sulfur-selenium gradient is lost as selenisation progresses. Accelerating voltage is 5kV and maximum diameter of interaction volume was estimated to be 170 nm. The Mo-L line and S-K lines cannot be resolved: the back Mo contact of the film can be identified by the sudden rise in the S signal.

2SSe10, indicating only a small quantity of selenide is within the laser penetration depth near the surface. The back/front contrast exists for short time selenisations, and is lost as selenide grows throughout the film in the longer selenisations. An increase in selenisation is always accompanied by a blue shift and broadening of the CZTS peak. These Raman results corroborate the SIMS results from Fig. 2 and EDX results from Fig. 3: for precursors, the selenide forms throughout the thickness of the film; for the sulfur pre-annealed samples, the CZTSSe selenide crystallises first near the back contact of the film, and forms throughout the film as the anneal progresses.

Figure 4: Raman spectra for all samples, for both the front and back surfaces. The CZTSSe peak is strong for the back side but weak for the front side in samples SSe10 and 2SSe10.

The 1.5° incidence angle GIXRD patterns for all samples are shown in Fig. 5, separated along the vertical axis for clarity. Of particular note are the CZTS **112** peak at $\sim 28.44^\circ$ [20] and the CZTSSe **112** peak between this peak and the selenide-only CZTSe position $\sim 27.16^\circ$ [21]; selenised samples show both peaks, indicating the existence of both CZTS and CZTSSe crystal structures. The spectra for ‘P’ and ‘S’ are close to identical: both show a broad peak between 45° and 60° , characteristic of precursor ‘pre-kesterite’ samples

Figure 5: GIXRD patterns for all samples, for an incident angle of 1.5° degrees.

that are not yet properly crystallised kesterite. This match in the samples' crystallinity as measured by GIXRD corroborates the similarity of their structure as observed by SEM, and indicates that any subsequent differences in selenisation are not the result of differing input crystal properties. The 'pre-kesterite' peak reduces steadily in amplitude with increasing selenisation time for samples 2SSe10 through 2SSe45, being replaced by the 204 and 116 peaks of CZTS and associated CZTSe peaks. This reduction in amplitude from 'pre-kesterite' to well resolved CZTS peaks indicates an increase in the degree of crystallinity of the film, and shows that the increasing degree of selenisation of the films observed by EDX is accompanied by recrystallisation.

4. Discussion

SIMS (Fig. 2), Raman spectroscopy (Fig. 4), and EDX showed that compound co-sputtered precursors selenise uniformly throughout the thickness of the film, even for very mild selenisation conditions. The slight gradient in selenium content measured by SIMS was not observed in EDX line scans, and not accompanied by a corresponding sulfur gradient. The slight SIMS gradient may merely be the result of lateral non-uniformity of selenide grain distribution over the large analysed diameter of the measurement [22]. In contrast to this chalcogen uniformity in depth, Qu *et. al.* produced a sulfide-selenide gradient in CZTSSe by selenisation of nanoparticle precursors and ascribed the gradient to the preferential selenisation of the surface exposed to the gas phase [15]. Furthermore, in our previous study of fully recrystallised CZTS, CZTSSe selenide grains nucleated around surfaces and CZTS grain boundaries, growing by removal of cations and sulfur from surrounding CZTS material [16]. Selenium gradients which could be clearly observed by EDX and X-ray diffractometry were produced by Salomé *et. al.* for stacked compound and metallic precursors [11]. These differences imply that the primary factors controlling the distribution of selenium in the CZTSSe resulting from selenium annealing are properties of the precursor, rather than only the of proximity of the surface of that precursor to the selenium gas phase.

Short time 425°C selenisations of sulfur pre-annealed films showed preferential crystallisation of the CZTSSe selenide near the back contact (Fig. 1). Sulfur-selenium gradients near the back contact were observed by SIMS (Fig. 2) and EDX (Fig. 3), and confirmed by back and front side Raman spectroscopy (Fig. 4). This gradient was selenide rich at the back to selenide-poor at the front, and if maintained in a fully recrystallised absorber would result in a quasi-electric field directing electrons away from the junction, hindering carrier collection. Upon further annealing, the chalcogen gradient was lost. At the longest annealing times studied, there was evidence of segregation of sulfide and selenide grains. GIXRD (Fig. 5) showed that progressive selenisation of the film was always associated with an increasing degree of crystallinity. Given the clear increase in back contact crystallinity and selenisation of sulfur pre-annealed then selenised films, the implication was that selenium was introduced in the recrystallisation itself, rather than by substitution into either the metastable precursor or CZTS grains.

Although the morphology as measured by SEM and crystallinity as measured by GIXRD for the precursor

and sulfur pre-annealed samples were similar, SIMS showed a difference in distribution of sodium at the back contact. The CZTSSe crystallisation was more rapid in parts of the film with higher sodium concentration. Sodium-assisted sintering of CZTSSe has been observed by other workers in solution processed films [23]. The mechanism proposed in that study was that of a liquid phase Na_2Se_x species supplying selenium to the growing CZTSSe crystal. The initial back-contact CZTSSe growth observed in the sulfur pre-annealed samples with high levels of sodium near the back contact suggests a similar sodium-assisted growth mechanism was dominant in this study. Since the selenium diffusion into the film is very rapid, selenium is available everywhere; but it is only in the presence of excess sodium that the rate of selenide crystal formation is increased.

The importance of this sodium assisted selenisation places practical restrictions on the introduction of chalcogen gradients in CZTSSe films starting from compound co-sputtered precursors. To make a useful band gap graded absorber layer, the precursor must fully recrystallise with an appropriate anion gradient, without segregation of sulfide and selenide phases into separate grains. If the introduction of sodium via NaF layers is used to guide the selenisation, sodium will diffuse through the film faster than the CZTSSe selenide will recrystallise, spreading the anion gradient out before the annealing is complete. CZTS sulfide and CZTSSe selenide grains may segregate during the annealing, requiring high temperatures and long annealing times to resolve completely into selenide grains. Furthermore, the distribution of sodium is important for the device performance itself, as it has been shown to enhance device performance by increasing the hole density and moving the acceptor level closer to the conduction band [24], consistent with the conjecture that its presence in the anneal enhances the concentration of V_{Cu} intrinsic shallow acceptors, as it is hypothesised to do in CIGS [25]. Any method of arresting the sodium spread during annealing to preserve the chalcogen gradient will likely have undesirable electronic effects. Reconciling the different contributions of sodium, the requirement for full absorber recrystallisation, and the necessity to imprint a chalcogen gradient likely places too many restrictions on the annealing process. **These restrictions limit the potential for a chalcogen gradient** to be introduced solely during the annealing step in the case of compound co-sputtered CZTS.

In this study, pure sulfide CZTS precursors and annealed films annealed in selenium produced CZTSSe selenides with approximately 20-40% sulfur, with the only supply of sulfur in the anneal coming from the film itself. This suggests some precursor chalcogen is retained through crystallisation, although this study provided no information about its mobility during annealing. An alternative approach to obtain chalcogen gradings in compound-sputtered CZTSSe without the need to control so many different factors in the anneal may be to sputter a sulfur-selenium gradient or step into the precursor. We believe such a ‘control of precursor’ approach to be a potentially more productive path for future investigations of chalcogen gradient formation in compound co-sputtered CZTSSe than attempting to introduce the gradient in the annealing step.

5. Conclusion

In this study, compound co-sputtered CZTS precursors and precursor-like films were annealed in selenium atmospheres. By doing so, we have gained some information about the factors limiting control of chalcogen gradients introduced in the annealing step of compound co-sputtered precursors. Selenisation and recrystallisation of the absorber occur in the same process, and this process is affected by the presence of sodium. The mechanism coupling sodium and selenide recrystallisation was tentatively identified as incorporation of selenium into the growing crystal via sodium selenide compounds. The difficulties in simultaneously controlling sodium distribution, selenium incorporation, and crystallisation in the annealing phase were discussed, and the production of graded precursors as an alternative approach recommended as the way forwards to achieving chalcogen gradings in compound sputtered CZTSSe.

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Cu₂ZnSn(S,Se)₄ Solar Cell Absorbers from Diffusion of Selenium into Annealed Cu₂ZnSnS₄ Absorbers

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Abstract—Small grain compound-sputtered Copper Zinc Tin Sulfide (CZTS) precursors and large grain recrystallized CZTS solar cell absorbers are annealed at sub-recrystallization temperatures in selenium atmosphere to promote selenium diffusion into the CZTS films. Grazing incidence x-ray diffraction and Raman spectroscopy show the presence of two distinct sulfide and mixed sulfide/selenide phases, with the selenide-like phase more prominent at the front surface of the absorber. Only a narrow range of sulfur-to-selenium ratios is observed in the sulfide/selenide phase. Secondary ion mass spectrometry profiles show a compositional sulfur-selenium gradient for samples annealed at 450°C. Scanning electron microscopy with energy dispersive X-ray spectroscopy reveals that the compositional gradient is formed by a spatial distribution of sulfide/selenide grains, embedded in the remaining sulfide absorber. Sulfur-selenium gradients within single absorber grains are not observed, indicating that the mixed sulfide/selenide phase nucleates and grows in competition with the existing sulfide phase, rather than forming by replacement of anions within existing crystals. IV and EQE measurements of devices fabricated from the selenized absorbers support this conclusion.

Index Terms—CZTSSe, diffusion, gradient.

I. INTRODUCTION

The share of global energy production supplied by photovoltaics (PV) is small but rising rapidly. The industry supplying PV modules continues to evolve faster than anticipated, and while silicon PV is the current dominant technology [1], the future of PV may grow more diverse with increasing total energy market share. In view of such a diverse future, it is desirable to investigate thin film solar cells based on low-cost earth-abundant materials. The Copper-Zinc-Tin-Sulfide/Selenide quaternary semiconductor absorber material (hereafter CZTSSe or CZTS for the pure sulfide) is of particular interest, because of both its abundant constituent materials and its anticipated similarities with the more mature copper-indium-gallium-selenide technology (CIGS).

High efficiency CIGS devices employ In-Ga composition grading at both the front and the back of the cell to modify the bandgap and to minimize recombination [2]. Such band gap and material tuning can reasonably be expected to be necessary in future high-efficiency CZTSSe devices. It is also important to understand how the peculiarities of the quaternary system, such as absorber/buffer band misalignment [3], deep defects within the absorber [4], band gap fluctuations from cation disorder defects [5], secondary-phases [6], and back-contact issues [7] might be affected by the presence of such a gradient.

The bandgap of CZTSSe varies from approximately 1.0 eV for the pure selenide to approximately 1.5 eV for the pure sulfide, and can be controlled by the partial substitution of one element for another. There have been a number of studies of CZTSSe absorbers where a sulfur/selenium [8]–[10] gradient within the absorber has been of note. In these studies, the S or Se gradient in the absorber results from the conditions of the anneal in which the CZTS is recrystallised [8], [9], or else experimental details on the introduction of the gradient are sparse [10]. In the CIGS system, it is known that good control over the material grading is important, and that the front grading in particular can even be detrimental under some circumstances [2], [11]. Modelling of CZTSSe systems also show sensitivity to the type, position, and extent of band gap grading [12]. During recrystallization of the absorber, there are many competing effects which may limit the control of the gradient. It is therefore desirable to study the introduction of a S/Se gradient at a temperature lower than that required to recrystallize the absorber.

Diffusion of selenium into CZTSSe has been the subject of only a limited number of studies. Harvey and co-workers determined that the activation energy to diffusion of Se into CZTSe was 0.5 eV, and showed that the rate of diffusion increases with increasing chalcogen partial pressure, implying a grain boundary mediated diffusion [13]. The selenization kinetics in CZTSSe absorbers prepared from nanoparticle inks were investigated by Qu *et. al.*, and were found to be dependent on nucleation and cation reordering processes rather than on anion diffusion from the gas phase [14]. Additionally, the time at 500°C to replace half the sulfur with selenium was found to be only 10 seconds, likewise implying extremely fast diffusion of Se into CZTS.

This study was conducted with a view to limit the diffusion of selenium into compound-sputtered CZTS absorbers as the first step to establishing a controlled anion composition gradient in the CZTSSe absorber. Selenium was diffused into both crystallized CZTS absorbers and their equivalent non-annealed precursors at temperatures low enough to limit the recrystallization process. In the first experimental series the temperature was varied between 350–450°C for fixed annealing time. In the second experiment series the temperature was fixed at 450°C and the annealing time varied between 10–30 minutes. The absorbers formed by selenization of pre-sulfurized and precursor samples were compared by grazing incidence x-ray diffraction (GIXRD), Raman spectroscopy, secondary ion mass spectrometry (SIMS) and scanning elec-

tron microscope energy dispersive X-ray spectroscopy (SEM-EDS). For the time series, solar cell devices were fabricated and characterized by current-voltage (I-V) measurements and external quantum efficiency (EQE) measurements.

II. EXPERIMENTAL DETAILS

Bilayer molybdenum back contacts were sputtered onto soda-lime glass substrates. $\text{Cu}_2\text{ZnSnS}_4$ precursor material was co-sputtered using a Lesker CMS-18 sputter system, in an Ar atmosphere from sulfur-compound targets CuS, SnS, and ZnS. Eight 2.5 cm x 2.5 cm precursors were fabricated simultaneously. Two separate precursor families were used for a selenization temperature dependence study, and for a selenization time dependence study.

For the temperature dependence study, the precursors had Cu/Sn ratios of 1.87 ± 0.02 and Zn/(Cu+Sn) ratios of 0.32 ± 0.02 , as determined by Rutherford back scattering-calibrated X-ray fluorescence measurements. Films were either denoted PSeT and retained as precursors prior to selenization, or denoted SSeT and sulfurized prior to selenization, for 'T' the selenization temperature. The SSeT samples were sulfurized in a pyrolytic carbon coated box with 40 mg of sulfur, between 580-590°C, and an Argon pressure of 351 Torr, for 10 minutes. Selenizations were performed in a separate graphite box loaded with 90 mg of selenium, at temperatures 350, 400, and 450°C, at an Ar pressure of 265 Torr, for 10 minutes. For each temperature, the PSe precursors and SSe sulfurized sample were selenized together.

For the time dependence study, the precursors had Cu/Sn ratios of 1.86 ± 0.02 and Zn/(Cu+Sn) ratios of 0.35 ± 0.02 . Time series samples were all sulfurized, under the same conditions as the SSe temperature series samples. Films were denoted 2S, 2SSe10, 2SSe20, and 2SSe30, for unselenized, and selenization times 10, 20, and 30 minutes respectively. For clarity, Table I lists the samples and their preparation conditions. Selenizations were performed under similar conditions to temperature series, in a coated box with 50 mg of selenium, at a temperature of 450°C. The mass of selenium in the box was reduced because a smaller box, fitting a single 2.5 cm x 2.5 cm sample, was used for the time series study. A portion of each sample was used to fabricate solar cell devices. Device portions of the films were etched in 5 wt% KCN for 2 minutes, rinsed in deionized water, then transferred to a CdS chemical bath. The chemical bath solution consisted of 1.1 M ammonia, 0.1 M thiourea, and 0.003 M cadmium acetate. Samples were kept in the bath for 495 seconds at 60°C to produce approximately 50 nm thick CdS buffer layers. The transparent front contact was deposited with RF-sputtering and consisted of a thin (80 nm) intrinsic ZnO and a thicker (210 nm) Al-doped ZnO layer.

Absorbers were characterized by GIXRD in a Siemens D5000 diffractometer. Raman spectroscopy was performed using a 532 nm laser in a Renshaw Invia spectrometer. SEM images and EDS maps were obtained using a Zeiss Leo 1550 device. SIMS depth profile measurements were performed using a Cameca IMS 7f instrument with a primary beam of

Figure 1. GIXRD diffractograms of the (1 1 2) peaks for samples PSeT and SSeT, for an incident angle of 1.5 degrees. Precursor and sulfurized samples are separated on the vertical axis for clarity, and each curve is normalized to its maximum count.

10 keV O_2^+ and an analyzed diameter of 60 micrometers. Devices were characterized by I-V using a Newport ABA Solar Simulator. Quantum efficiency (QE) measurements were performed in a home-made setup calibrated by externally measured Hamamatsu Si and InGaAs solar cells.

III. TEMPERATURE SERIES

The GIXRD diffractograms for samples SSeT and PSeT, from around the (1 1 2) CZTS(Se) peak and for an angle of incidence of 1.5°, are shown in Fig. 1. For the precursor PSe samples, the lower angle mixed selenide (CZTSSe) peak is extremely low amplitude at 350°C. It becomes more significant by 400°C, and is located at $\sim 27.52^\circ$ compared to the sulfide peak at $\sim 28.44^\circ$ [15]. At 450°C, the sulfide peak has disappeared entirely and the selenide peak is located at $\sim 27.68^\circ$. For the pre-sulfurized SSe samples, there is no lower angle selenide peak at 350°C, and at 400°C the selenide peak is still very low in relation to the sulfide peak. At 450°C, the selenide and sulfide peaks are of comparable amplitudes, and the selenide peak appears at $\sim 27.62^\circ$. Following the method of Salomé *et al.* [9], the shift of the mixed phase selenide peak from the 'pure' CZTSe position of 27.16° was used to estimate a Se/(S+Se) ratio. For samples PSe400, PSe450, and SSe450, these ratios were 0.72, 0.59, and 0.64, respectively.

The GIXRD diffractograms for angles of incidence between 1 and 10 degrees for sample SSe450 are presented in Fig. 2. The ratio of the sulfide to selenide (S / Se) peak amplitude is shown in the inset. It is clear that the selenized

TABLE 1
SAMPLE TABLE

Series	Sample	Elemental ratios		Sulfurization Conditions			Selenization Conditions		
		Cu/Sn	Zn/(Cu+Sn)	Temperature	Time	Ar pressure	Temperature	Time	Ar pressure
Temperature	PSe350	1.87±0.02	0.32±0.02	-	-	-	350°C	10 min	265 Torr
Temperature	PSe400	1.87±0.02	0.32±0.02	-	-	-	400°C	10 min	265 Torr
Temperature	PSe450	1.87±0.02	0.32±0.02	-	-	-	450°C	10 min	265 Torr
Temperature	SSe350	1.87±0.02	0.32±0.02	580°C	10 min	350 Torr	350°C	10 min	265 Torr
Temperature	SSe400	1.87±0.02	0.32±0.02	580°C	10 min	350 Torr	400°C	10 min	265 Torr
Temperature	SSe450	1.87±0.02	0.32±0.02	580°C	10 min	350 Torr	450°C	10 min	265 Torr
Time	2SSe10	1.86±0.02	0.35±0.02	580°C	10 min	350 Torr	450°C	10 min	265 Torr
Time	2SSe20	1.86±0.02	0.35±0.02	580°C	10 min	350 Torr	450°C	20 min	265 Torr
Time	2SSe30	1.86±0.02	0.35±0.02	580°C	10 min	350 Torr	450°C	30 min	265 Torr
Time	2S	1.86±0.02	0.35±0.02	580°C	10 min	350 Torr	-	-	-

Figure 2. GIXRD diffractograms of the (1 1 2) peak for sample SSe450, for incident angles between 1 and 10 degrees. Inset: the ratio of the sulfide/selenide (S/Se) peak amplitudes, showing a more sulfide-like character deeper into the film.

absorber's character is more 'sulfide-like' for deeper angles of incidence. The position of the selenide peak does not change substantially, indicating that the Se/(S+Se) ratio within the selenide does not change with depth. That the selenide peak is distinct and not broad compared to the sulfide, and that the S/Se ratio does not change with depth indicates the presence of distinct selenide and sulfide phases. There is no evidence of a selenide with a spatially graded composition.

The Raman spectra for the temperature series are shown in Fig. 3. For PSe350, a low broad peak at $\sim 255 \text{ cm}^{-1}$ appears in addition to the higher wavenumber, CZTS-like peaks of the original precursor. At 400°C the CZTSSe peak at approximately 210 cm^{-1} is present and comparable in amplitude to the main CZTS peak at 338 cm^{-1} [16], and has a clear low wavenumber shoulder at $\sim 185.5 \text{ cm}^{-1}$ that may be SnSe_2 [17]. There is still a low peak as for PSe350, but it is located at $\sim 245 \text{ cm}^{-1}$. This low peak is difficult to

assign, but may be MoSe_2 (245 cm^{-1}), ZnSe (250 cm^{-1}), or a-Se (255 cm^{-1}) [18]. For the pre-sulfurized samples SSeT, there is no significant secondary phase or CZTSSe formation at 350°C. Aside from the CZTS peak and the positioning of the low peak around $245\text{--}255 \text{ cm}^{-1}$, the Raman spectra for 400 and 450°C are similar for both pre-sulfurized SSeT and precursor PSeT samples. By the method of Salomé *et al.* [9], the peak shift of the CZTSSe peak from 197 cm^{-1} for a selenium-only CZTSe phase to 210 cm^{-1} gives a Se/(S+Se) ratio of 0.65, in agreement with the GIXRD data. For the pre-sulfurized samples, the main CZTS peak becomes more broad and shifts to lower wavenumber as selenization temperature increases, indicating a reduction in uniformity of the sulfide phase.

SIMS data for pre-sulfurized samples SSe400 and SSe450 are shown in Fig. 4. All samples show a peak in ^{80}Se near the ^{98}Mo cut-off, indicating the formation of MoSe_2 , in accord with previous studies showing rapid diffusion of Se through CZTS and CZTSe [13], [14]. The higher base count of ^{80}Se in SSe450 compared to SSe400 is in accordance with the more significant selenide peak in the GIXRD diffractograms. For SSe450 only, there is a complementary compositional gradient in both ^{80}Se and ^{32}S towards the front of the film (low sputter time), with Se increasing and S decreasing towards the surface. In both samples, increases in Se concentration are correlated with an increased ^{23}Na concentration. There is also a slight apparent drop in ^{63}Cu and ^{68}Zn that may be related to the presence of SnSe_2 or by a matrix effect depression of the sputtering rate of these cations caused by the presence of selenide phases. Of all of the temperature series samples, only SSe450 shows this S/Se compositional gradient to any significant extent.

The GIXRD data for SSe450 show a single S/Se ratio within the selenide; the SIMS data shows a gradient in the film. This apparent contradiction is resolved by consideration of film morphology and the distribution of Se measured by SEM-EDS. The progression of SEM cross-section images in Fig. 5 (a-c) show the structural evolution of the precursors PSeT and Fig. 5 (d-f) the pre-sulfurized samples SSeT with increasing selenization temperature. PSe350 and SSe350 appear structurally very similar to their unselenized equivalents (not included). Some limited recrystallization has occurred in PSe400, although the columnar precursor structure is still

Figure 3. Raman spectra for samples PSeT and SSeT. Peak positions for CZTS, CZTSSe, and for possible secondary phase SnSe₂ are labelled. The three unlabelled, closely spaced red lines are for MoSe₂ (245 cm⁻¹), ZnSe (250 cm⁻¹), and a-Se (255 cm⁻¹). The labelled peak position of 210 cm⁻¹ for CZTSSe is for a S/(S+Se) ratio of 0.35. Samples are separated on the vertical axis for clarity.

partially preserved. PSe450 has recrystallized further, but still has very small grains compared to the pre-sulfurized samples. For SSeT, only a small increase in grain surface roughness is observed going from 350 to 400°C selenization. It is not until 450°C that a significant morphological change occurs, with a distinctly two-toned composition of rough surface grains and smooth, large grains close to the back Mo contact. All of the samples show a 50-100 nm layer of MoSe₂ present at the back contact, in accord with the SIMS results.

SEM-EDS maps of sample SSe450 for Cu L, S K, and Se L series, shown in Fig. 6 (b-d) with accompanying SEM image (a), elucidate the origin of the two-tone structure and resolve the apparent contradiction between the distinct sulfide/selenide GIXRD peaks and compositional SIMS S/Se gradient. The Cu EDS map (b) is relatively uniform, and the Zn and Sn signals (not included) are similarly so. The S and Se maps are not, and show a slightly increased density of S in regions where there are large voids in the Se map. The Se map provides the most clarity, showing grains or regions of grains with and without Se. The boundaries between Se containing regions and regions without Se are quite distinct. There are more S-rich grains towards the back contact and more Se-containing grains towards the front. This tendency for single-composition selenide grains to be arranged towards

Figure 4. SIMS profiles for pre-sulfurized samples (a) SSe400 and (b) SSe450.

the front of the film manifests as a continuous gradient when measured over the 60 micrometer analyzed diameter of the SIMS.

IV. TIME SERIES

Normalized GIXRD diffractograms for the time series 2SSe are shown in Fig. 7. As for the temperature series, there are two distinct peaks corresponding to the mixed selenide CZTSSe phase (27.65°) and the CZTS phase (28.45°). As the selenization time increases from 10 to 20 to 30 minutes (samples 2SSe10-30), the selenide peak does not shift in angle, but becomes larger in relation to the sulfide peak. Shown in the inset of Fig. 7 are the ratios of the sulfide/selenide peak amplitudes for each selenized sample. With increasing selenization time, the amount of sulfide remaining in the film is reduced, and the contrast in sulfide/selenide ratio from the front to the back of the film (shallow to deep angles) is reduced. That is, the spatial distribution of remaining sulfide phase becomes more uniform as it is replaced with selenide.

These results are in accord with SEM-EDS data in Fig. 8 (a-c), which show the SEM cross sections, with the grain structure growing more uniform with increasing selenization

Figure 5. SEM cross-section images of samples (a) PSe350; (b) PSe400; (c) PSe450; (d) SSe350; (e) SSe400; and (f) SSe450.

Figure 6. Sample SSe450, (a) SEM cross-section and corresponding EDS maps for (b) Cu L series; (c) S K series (not resolved from Mo L series); and (d) Se L series.

Figure 7. GIXRD diffractograms of the (1 1 2) peaks for samples 2SSe10-30 and 2S, for an incident angle of 1.5 degrees. Inset: the ratio of the sulfide/selenide (S/Se) peak amplitudes for the three selenized samples.

Figure 8. SEM cross-section and corresponding Se L series EDS map for (a, d) 2SSe10; (b, e) 2SSe20; and (c, f) 2SSe30.

time. There is some evidence of surface decomposition for the thirty minute selenization, 2SSe30, as the surface becomes less flat than for 2SSe20. Fig. 8 (d-f) show the corresponding EDS maps for the Se L series. For 2SSe10 as for SSe450, there are large sulfide grains through the film and a higher density of sulfide closer to the back contact. For 2SSe20, these sulfide grains have been greatly reduced in size. By the thirty minute selenization of 2SSe30, the remaining sulfide grains are very small, and there is no easily discernable pattern in their distribution through the thickness of the film.

Device results from the time series are shown in Fig. 9 (a-c), and corresponding short-circuit external quantum efficiency measurements in Fig. 9 (d). Fill factors are not included for brevity. The reference sulfide devices 2S are 6% efficient. In contrast, devices 2SSe10 are less than 4% efficient, with lower than expected J_{sc} and V_{oc} values. V_{oc} and J_{sc} recover somewhat with increasing selenization time. The low current for 2SSe10 is reflected in a poor long wavelength collection in the QE. This is partially recovered with increasing selenization time. The absolute EQE level also increases with increasing anneal time. With increasing selenization time, the reduced recombination from V_{oc} data and increased generation/collection from J_{sc} data point to an increasing selenide crystal size and uniformity. These data support the inference that selenide grains nucleate and grow at the expense of sulfide grains.

V. CONCLUSION

Even the large CZTS grains of pre-sulfurized absorbers did not materially arrest the diffusion of selenium through the thickness of the films, in accord with related studies [13], [14]. Rather, GIXRD and Raman data indicated that larger CZTS grains inhibit nucleation and growth of selenide grains. The S/Se ratio of these grains was uniform under the conditions of the ‘low temperature’ selenizations of this study, and the apparent compositional gradient measured by SIMS was shown by SEM-EDS to be the result of a non-uniform distribution of selenide grains through the thickness of the films. SEM-EDS maps of absorbers selenized for longer times showed that the selenide grains grow at the expense of the sulfide grains, rather than by slow diffusion of selenium into existing sulfide grains. Devices fabricated from incompletely selenized absorbers displayed poorer collection, supporting this conclusion. The selenide grains showed a tendency to nucleate towards the surface of the film, but further study is required to determine the cause and consistency of this behaviour.

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Figure 9. Device characteristics for the time series: (a) efficiency; (b) J_{sc} ; and (c) Open circuit voltage V_{oc} . (d) External quantum efficiency for the time series.

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Secondary ion mass spectrometry as a tool to study selenium gradient in $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$

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Secondary ion mass spectrometry (SIMS) has been utilized to study compositional gradient in compound-sputtered and annealed $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe). SIMS image depth profiling shows a non-uniform spatial distribution of selenium, while sulfur is more evenly distributed, and supports a mechanism where selenization is accompanied by grain growth rather than substitution of selenium for sulfur. Furthermore, SIMS depth profiles by O_2^+ primary ions detecting element, M, and by Cs^+ primary ions detecting MCs^+ have been compared, where a linear relationship between the sulfur and the selenium concentration is observed for concentrations in the range of $\text{Se}/(\text{S}+\text{Se})$ ratio from 0.25 to 0.65.

3D image of the spatial Se and S distribution in a $20 \times 20 \mu\text{m}$ grid measured with SIMS image depth profiling. Add grid?

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1 Introduction Kesterite $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe), is a promising material for the use as the p-type absorber layer for thin film solar cell applications based on earth abundant elements. One potential method to increase the efficiency of thin film solar cells with CZTSSe is to utilize a varying $\text{Se}/(\text{S}+\text{Se})$ ratio similar to the $\text{Ga}/(\text{In}+\text{Ga})$ grading that has been successfully applied in $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ (CIGS) solar cells [1]. Sulfide $\text{Cu}_2\text{ZnSnS}_4$ has a band gap of around 1.5 eV, while selenide $\text{Cu}_2\text{ZnSnSe}_4$ has a band gap of around 1.0 eV [2]. Hence, the band gap of CZTSSe depends strongly on the $\text{Se}/(\text{S}+\text{Se})$ ratio. Several studies have reported a compositional gradient in CZTSSe [3–7], but issues remain before a controllable band gap grading can be implemented in commercial cells [8]. In particular, a grain growth has been shown to accompany the selenization, resulting in a nonhomogeneous lateral distribution [8]. The $\text{Se}/(\text{S}+\text{Se})$ ratio has been studied using characterization

methods including scanning electron microscope with energy dispersive x-ray spectroscopy (SEM-EDX) [3,6,7], grazing incidence x-ray diffraction (GIXRD) [4,7] and secondary ion mass spectrometry (SIMS) [4,7]. The advantage of SIMS is that it provides superior detection sensitivity and a precise depth resolution. However, the depth profile analyses rely on constant ionization efficiency with depth and are usually performed over a large area, showing the average two dimensional (2D) distribution of each element. As a result, the lateral information is lost, which is of particular importance for multicrystalline structures such as CZTSSe, where the chemical composition within the grains may differ from the averaged composition [7]. In order to study this non-uniform distribution with SIMS one can measure the three dimensional (3D) chemical information with high spatial resolution. This can be accomplished with SIMS image depth profiling, where infor-

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Table 1 Experimental conditions of the three SIMS measurements performed a CZTSSe sample.

Experimental conditions	O_2^+ image depth profile	O_2^+ depth profile	MCs+ depth profile
Primary ions	O_2^+	O_2^+	Cs^+
Current	20 pA	100 nA	20 nA
Raster size	$20 \times 20 \mu\text{m}$	$150 \times 150 \mu\text{m}$	$200 \times 200 \mu\text{m}$
Analyzed area	$20 \times 20 \mu\text{m}$	62 μm diameter	62 μm diameter
Impact energy	10 keV	10 keV	5 keV
Angle of incidence (off the surface normal)	52.5°	52.5°	XX°
Detected ions	$^{32}\text{S}^+$ and $^{80}\text{Se}^+$	$^{32}\text{S}^+$, $^{80}\text{Se}^+$ and $^{98}\text{Mo}^+$	$^{32}\text{S}^{133}\text{Cs}^+$, $^{80}\text{Se}^{133}\text{Cs}^+$ and $^{98}\text{Mo}^{133}\text{Cs}^+$

mation on the position of the secondary ions is preserved while sputtering. The result is a set of images acquired from different depths. Moreover, the compositional gradients measured by SIMS may deviate from the actual compositional gradient due to a matrix effect. This may occur since the ionization probability of each element depends on the compositional matrix that is sputtered. However, it is possible to minimize the matrix effect by detecting MCs⁺ secondary ions. when sputtering with Cs⁺ primary ions, where M is the element to be analyzed [9–12]. Previously, both positive secondary ions with O₂⁺ primary ions and MCs⁺ ions with Cs⁺ primary ions have been utilized for SIMS analysis of CZTS(Se) [13–16]. In this paper, we perform image depth profiling for CZTSSe and show that a non-uniform distribution of S and Se can be detected for different depths by SIMS. Furthermore, we measure O₂⁺ depth profile and MCs⁺ depth profile and compare between each method to evaluate the impact of the matrix effect for CZTSSe, and to further determine which experimental conditions to use for compositional depth analysis.

2 Experimental The samples studied was deposited by co-sputtering of compound precursors CuS, ZnS and SnS on a Mo-coated substrate followed by two annealing processes. O₂⁺ image depth profiling was performed on a sample which was annealed at 500°C for 10 minutes in a sulfur-rich atmosphere, causing the growth of Cu₂ZnSnS₄ grains. This was followed by another anneal at 425°C for 45 minutes in a selenium-rich atmosphere to incorporate Se into the grains and thus creating a Se gradient. The O₂⁺ and CsM⁺ depth profiling was performed on a similar sample where the first annealing temperature was 580°C and the second was 450°C, both at 10 minutes. More detailed information about the sample processing can be found elsewhere [8]. The SIMS results have been obtained using a magnetic sector Cameca IMS-7f ion microprobe. Three measurements were performed with different experimental conditions, as listed in Table 1, where the O₂⁺ ion beam was utilized for image depth profiling. SEM-EDX images were taken with a Zeiss Leo 1550 using a 5kV accelerating voltage. The depth was calibrated with the SEM and a constant erosion rate was assumed when converting sputtering

Figure 1 (a) Se L α SEM-EDX map of the first sample (b) corresponding SIMS depth profile.

3 Results and discussion Figure 1 shows a cross-sectional SEM-EDX map of the Se content in the CZTSSe film (Fig. 1(a)), and the corresponding depth profile as measured by SIMS. The grain sizes as observed by SEM (not shown) are around 200 nm, and from Fig. 1(a) it is evident that the Se is non-uniformly distributed and that the Se rich areas are larger than grains. The SIMS depth profile, (Fig. 1(b)), on the other hand shows the average Se and S intensities where local variations are missing. Figure 2 shows the $^{80}\text{Se}^+$ signals from the SIMS image depth profiling taken at four different depths, where d indicates the approximate distance to the surface of the absorber. The images (Fig.2) clearly shows a non-uniform Se distribution, where selected areas with a higher Se signal are marked by (i), (ii) and (iii).

Regions (i) and (ii) appear to be Se-rich zones, likely from a small set of grains, similar to that observed in Fig. 1(a). However, regions (i) and (ii) are not Se-rich at larger depths, while other areas contain more Se (e.g. region (iii)). This confirms the non-uniformity of the Se distribution and supports that only some set of grains contain high amount of Se, most likely due to growth of selenide grains. The S signals for identical depths are shown in Fig. 3. This shows a more uniform distribution where the intensity is increasing with depth. This is to be expected given that the S content was uniformly distributed before the introduction of Se.

Figure 2 $^{80}\text{Se}^+$ signal acquired with SIMS image depth profiling at four different distances to the surface; (a) 20 nm, (b) 100 nm, (c) 250 nm and (d) 350 nm, and with a raster of $20 \times 20 \mu\text{m}$.

The result is also similar to SEM-EDX for the S K α 1 signal for the sample (not shown). In Fig. 3(c) a dark region for the $^{32}\text{S}^+$ signal (iv) correlate well to high signal of $^{80}\text{Se}^+$ in Fig. 2(c) (region (iii)), which indicates that the Se grows at the expense of S. The accumulated signal from the images at each depth results in equal signal normalized to the O_2^+ depth profile over a much larger rastered area.

To overcome the dependence on the matrix of the ionization efficiency of an element, a Cs^+ cluster approach have successfully been applied in several materials [9–12]. To explore the potential use in CZTSSe films, both elements M secondary ions using O_2^+ primary beam and MCs^+ secondary ions using Cs^+ primary beam have been compared. The O_2^+ depth profile is shown in Fig. 4 and the MCs^+ depth profile is shown in Fig. 5. To simplify the analysis of the results, the measured points in the CZTSSe layers are divided into three regions; (I) close to the surface, (II) the middle of the sample and (III) close to the Mo back contact. Both measurements show a change in S and Se signal with depth. The Se gradients appear to form at the expense of the sulfur signals which indicate that there are exchanges of Se with S in the matrix. Additionally, the Mo signals are increasing in the CZTSSe region which is most likely due to an interference with the sulfur signal ($^{32}\text{S}^{66}\text{Zn}^+$ for instance). To investigate if the ratio $\text{S}/(\text{S}+\text{Se})$ is kept constant with depth, the Se signals have been plotted as a function of S signals in the insets in Fig. 4 and Fig. 5 with the O_2^+ and Cs^+ source, respectively. Similar correlation plots have been made for CIGS [12] and III-V semiconductors [17].

Figure 3 $^{32}\text{S}^+$ signal acquired with SIMS image depth profiling at four different distances to the surface; (a) 20 nm, (b) 100 nm, (c) 250 nm and (d) 350 nm, and with a raster of $20 \times 20 \mu\text{m}$.

If the signals have a linear dependence, the actual concentration ratio between S and Se can be estimated [12]. The plotted points from region II (black points) show a linear dependence for the $\text{S}/(\text{S}+\text{Se})$ ratio for both sources. However, the plotted points from regions I and III (gray points) deviate from this linear dependence. The deviation appears to be an offset for the O_2^+ depth profile while for the MCs^+ depth profile it appears to be exponential. The $\text{Se}/(\text{S}+\text{Se})$ ratios for region II are calculated using the intensities of S and Se, and the slope in the insets in Fig. 4 and Fig. 5. The ratio is varying from 0.65 to 0.35 for the O_2^+ depth profile and from 0.55 to 0.25 for the MCs^+ depth profile. The latter is closer to what one could expect from an SEM-EDX line scan (not shown). The deviation from linear dependence in regions I and III could be the result of either two origins; (1) the high content of Se in region I and S in region III causes a matrix effect or (2) the formation of secondary phases and elemental S or Se causes the total atomic concentration of $\text{S} + \text{Se}$ to change and consequently the linear relationship is not valid regardless of the matrix effect. If one assumes that the concentration of secondary phases increases towards the back contact and the surface, which is in agreement with previous results [13,18,19] and more elemental Se exists near the surface due to smaller grains and more grain boundaries. Consequently, (2) is a valid explanation taking into account that the intensity of Se increases more compared to S towards the surface while the opposite occurs towards the back contact (from the inset figures). This may give a physical explanation for the deviation in regions I and III.

Figure 4 O_2^+ depth profile of CZTSSe and into the Mo back contact. The vertical lines at about 150 and 550 nm separate the three regions I, II and III of the CZTSSe layer and the vertical line at 900 nm indicates the estimate for the back contact. Inset: corresponding intensity of Se as a function of intensity of S from region II (black) and regions I and III (gray). The solid line is the linear fit from region II.

The deviation could also originate from the matrix effect (1) in these regions. In the case for Ga and In in CIGS it has been shown that detecting MCs^+ ions removes the matrix effect, but not if the matrix elements, M, are detected [12,20]. It has also been shown that the reduction of the matrix effect using MCs^+ depends on the amount of Cs^+ ions available compared to matrix elements and the sample material [21]. This can be achieved with a high sputtering yield by either increasing the impact angle or energy of the primary ion beam. The sputtering yield for the MCs^+ depth profile was calculated to 1.5, which is significantly lower than recommended [21] and is a reason why the matrix effect cannot be excluded. Further studies of utilizing SIMS to investigate Se gradient will be performed.

4 Conclusion The use of SIMS has been studied on a CZTSSe absorber with a Se gradient. A non-uniform spatial distribution of Se with depth has been detected with SIMS imaging depth profile, which correlates well with previous SEM-EDX results. This confirms that SIMS image depth profiling is a method that can be used to gain additional knowledge about the spatial composition in polycrystalline CZTSSe.

Figure 5 MCs^+ depth profile of CZTSSe and into the Mo back contact. The vertical lines at about 210 and 650 nm separate the three regions I, II and III of the CZTSSe layer and the vertical line at 900 nm indicates the estimate for the back contact. Inset: corresponding intensity of Se as a function of intensity of S from region II (black) and regions I and III (gray). The solid line is the linear fit from region II.

Furthermore, elemental ions, M, detected utilizing an O_2^+ ion beam and MCs^+ cluster ions detected utilizing a Cs^+ ion beam have been compared with each other to examine the impact of the matrix effect on the corresponding measurement modes. The results show that both configurations have low matrix effect far from any interfaces, however, close to the surface or The back contact there exist either matrix effects or an abundant amount of secondary phases and elemental formation.

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