

Voids in Kesterites and the Influence of Lamellae Preparation by Focused Ion Beam for Transmission Electron Microscopy Analyses

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Abstract—Kesterite solar cells based on $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) are potential future candidates to be used in thin-film solar cells. The technology still has to be developed to a great extent and for this to happen, high levels of confidence in the characterization methods are required, so that improvements can be made on solid interpretations. In this study, we show that the interpretations of one of the most used characterization techniques in kesterites, scanning transmission electron microscopy (STEM), might be affected by its specimen preparation when using focused ion beam (FIB). Using complementary measurements based on

scanning electron microscopy and Raman scattering spectroscopy, compelling evidence shows that secondary phases of ZnSe mixed in the bulk of CZTSe are the likely cause of the appearance of voids in STEM lamellae. Sputtering simulations support this interpretation by showing that Zn in a ZnSe matrix is preferentially sputtered compared with any metal atom in a CZTSe matrix.

Index Terms— $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ (CZTSSe), focused ion beam (FIB), kesterite, thin-film solar cells, transmission electron microscopy (TEM).

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I. INTRODUCTION

THE semiconductor $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ (CZTSSe), with kesterite crystalline structure, is currently studied as the absorber layer in thin-film solar cells. The biggest selling point of the CZTSSe compound has been the use of abundant materials like Cu, Zn, and Sn [1]. Some other advantages of the CZTSSe compound are: its tuneable bandgap energy from ~ 1 [2], [3] to 1.5 eV [4] (by replacing Se by S); the high value of optical absorption [5], [6]; the use of a solar cell structure similar to the one of $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ [7], [8]; some doping properties can be achieved by diffusion of alkalis from the glass [9]; the flexibility in having several methods capable of synthesizing the compound [10]–[18]; just to name a few. In spite of these advantages, the maximum power conversion efficiency of a CZTSSe laboratory solar cell is just around 12.6% [19]. Such limited efficiency has been attributed to a few issues which significantly limit the open circuit voltage (V_{oc}): secondary phases [20]–[25]; poor band alignments and cell architecture problems [15], [16], [26], [27]; high values of fluctuating potentials [28]–[31]; and a kesterite/stannite crystal mixture [32]–[34]. Among all these issues, secondary phases have been intensively studied as they form easily [23], [35]–[37] and are detrimental from an electrical point of view. Raman spectroscopy, X-ray diffraction (XRD), and scanning transmission electron microscopy (STEM) are the most frequently used techniques to identify these spurious phases. In particular, STEM analysis is quite relevant as it allows for an evaluation of the morphology, crystallinity, and of the sample's elemental composition (by energy-dispersive X-ray spectroscopy—EDS). Commonly, the preparation of the STEM lamellae is done either by a combination of mechanical and Ar^+ ion polishing or by milling with a Ga^+ focused ion beam (FIB). State-of-the-art FIB tools are capable of sample preparation with the advantage of fast and precise milling of

the lamellae, with very limited damage to the lamellae surface by finishing the milling with low ion beam energy (0.5–2 keV). However, even in these cases, the ion milling process might create artifacts in some material systems.

In this paper, we present a study showing that the preparation of STEM specimens by using FIB sample preparation might lead to the appearance of artifacts in the STEM characterization of $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) samples. There is evidence that voids in the lamellae observed in STEM analysis could be artifacts created by the presence of ZnSe secondary phases in the CZTSe sample. We use a combination of STEM, Raman spectroscopy, scanning electron microscopy (SEM), and sputtering simulations to support these findings.

II. EXPERIMENTAL

Solar cells were fabricated on a 3-mm-thick, 25-cm² soda lime glass (SLG) substrate covered by 400 nm of molybdenum (Mo) as electrical back contact. Metallic precursors were sequentially deposited using e-beam evaporation and selenized at 460 °C in a Se-rich atmosphere to form the CZTSe layer as described elsewhere [38]. This particular set of samples had a 100-nm-thick SiO_2 layer sputtered on top of the SLG to prevent alkali diffusion [9]. The CZTSe absorbers were then finished into solar cells with a CdS layer deposited by chemical bath deposition and a transparent conductive oxide constituted by *i*-ZnO and ZnO:Al. The final solar cell structure was: SLG/ SiO_2 /Mo/CZTSe/CdS/*i*-ZnO/ZnO:Al and the device studied here had a power conversion efficiency of 5.3%. We note that on top of Mo, a layer of MoSe_2 is usually formed [39].

STEM images were taken with an FEI Titan ChemiThemis 80–200 kV Cs-probe corrected transmission electron microscope, operating at 200-kV accelerating potential and equipped with electron Bruker EDS SuperX detector. In this method, a coherent focused probe scans across the specimen and the X-ray emission spectrum is recorded in each probe position. All samples studied in the cross-sectional mode were prepared in a FIB FEI Dual-Beam Helios 450 S with FIB lift-out Mo-grids using a technique known as “lift-out” [40]. On top of the solar cell, we deposit a carbon layer to reduce the charging effect that displaces the electron/ion beam during the Pt bi-layer deposition. The Pt deposition assisted by the electron and the Ga beam serves to reduce the vertical ripples (either curtain effect or waterfall effect) [41]–[43] due to changes in the sputter yield and angle of incidence as the ion beam passes over a step, pore, local curvature, or regions of different compositions. The lamella ion-milling, i.e., the polishing process, was done using a Ga^+ beam with 30-15-2–1 kV polishing steps to thin down the lamella and final polishing energy of 1 kV to minimize lamella surface damage. SEM images were taken with a high-resolution NovaNanoSEM 650 SEM system. Raman scattering experiments were carried out at room temperature using a Jobin-Yvon LabRaman HR800 spectrometer equipped with a multi-channel Peltier-cooled charge-coupled device detector, in the backscattering geometry, and using a 442-nm excitation wavelength. The sample surface was focused with an objective of $50\times$ (numerical aperture = 0.50; working distance = 10.6 mm), and the incident power was varied from 70 to 790 μW .

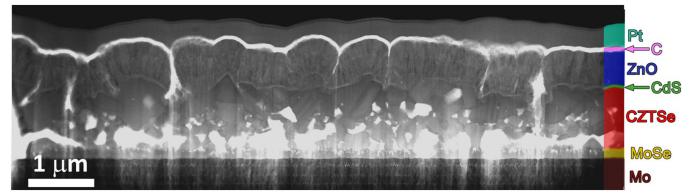


Fig. 1. STEM BF image of the cross section of a CZTSe solar cell. The white spots are voids in the CZTSe film, whereas the top continuous white layer is the protective carbon coating.

III. RESULTS

A bright field (BF) cross-sectional image of the CZTSe lamella is shown in Fig. 1. The image shows, from bottom to top, the Mo rear electrode (deposited with four layers), an MoSe_2 layer, the CZTSe absorber, the CdS buffer layer, the ZnO transparent conductive layers, a thin and bright protective carbon layer, and then another protective Pt layer deposited by the FIB. In STEM BF images, bright areas either correspond to very low mass density regions (e.g., the protective carbon layer) or to voids/empty spaces where the lamella is highly transparent to the incoming beam. That is the case of the low mass density protective carbon layer. The ZnO layer presents some vertical white segments, corresponding to either cracks or pin-holes in the film. Other bright areas or pin-holes can be observed in the CZTSe layer. The identification of such pinholes is important as they are detrimental from a device point of view. The observation of voids in the growth of kesterite materials is something that is common and it has been attributed mostly to Kirkendall effects during the chalcogenation process [44]–[46] and to complex thermodynamic reactions taking place at the Mo interface [47]. As such, the voids seen in the literature have the tendency to be present close to the back contact. In our case, although voids are present close to the Mo interface, they are also present, to some extent, throughout the whole thickness of the CZTSe layer.

To validate the presence of the voids and to analyze the sample elemental distribution, we performed high-angle annular dark field (HAADF) imaging and EDS analysis. Fig. 2(a) shows a HAADF image of the same region of the lamella. The voids and the protective carbon layer now show a dark contrast. EDS mappings for Sn, Cu, Zn, Se, Cd, and S for the same region are also presented. Cu and Sn are distributed equally inside the CZTSe but not uniformly, as there are spots with no counts. For the Zn and Se EDS maps, we can still see dark areas, corresponding to voids. There is also a high intensity of Zn and Se signals close to the voids. The high concentration of Zn in the top layers corresponds to the ZnO layer. In the CZTSe layer, a bright spot in the BF image (or dark in the HAADF image) could be related both with a void or with a lower atomic number phase like ZnSe, since Sn ($Z = 50$) is a much heavier element than Cu ($Z = 29$), Zn ($Z = 30$), and Se ($Z = 34$). Thus, a ZnSe region would appear as a much lighter elemental region than a $\text{Cu}_2\text{SnZnSe}_4$ region. The EDS analysis shows that parts of the dark regions in the HAADF image are indeed Zn-rich areas, and it also shows that close to these regions, there are areas with no EDS signal of any element, confirming the presence of voids. The non-uniform distribution of Zn and Se with the presence of

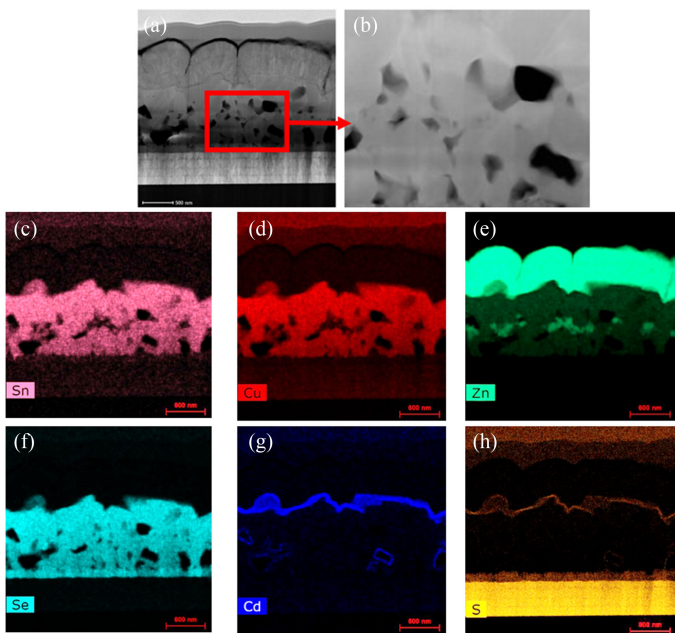


Fig. 2. (a) and (b) HAADF image and corresponding STEM-EDS maps for (c) Sn, (d) Cu, (e) Zn, (f) Se, (g) Cd, and (h) S. The analysis confirms voids in the sample with a slight enrichment of ZnSe in adjacent regions. The high concentration of S at the back contact is due to superimposition with Mo.

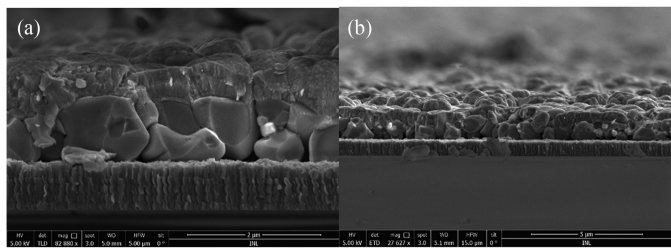


Fig. 3. High- and low-magnification SEM images of the cross section of the CZTSe solar cell.

ZnSe aggregates close to the voids is the first indication that the two events can be to a certain degree correlated. Furthermore, the EDS analysis also shows that a small number of visible voids are surrounded by Cd and S, suggesting a layer of CdS. This fact can be explained by these specific voids being already present during the chemical bath deposition of the CdS layer. On the voids where Cd and S are present, the concentration of Zn is similar to the rest of the film. Hence, this analysis reveals the possibility of two different types of voids: i) voids that were already present at the sample preparation stage and that were identified by being coated by a CdS layer; ii) voids that are close to the segregation of ZnSe aggregates. In the rest of the paper, we will focus our attention on the second type of voids, i.e., the ones in the vicinity of ZnSe aggregates.

To verify if the voids that are not coated in CdS are present in the samples prior to the FIB process, we prepared cross sections by cleaving the samples and performing SEM measurements. A representative image of the cross section is shown in Fig. 3. The image shows the same layers as previously but surprisingly, the

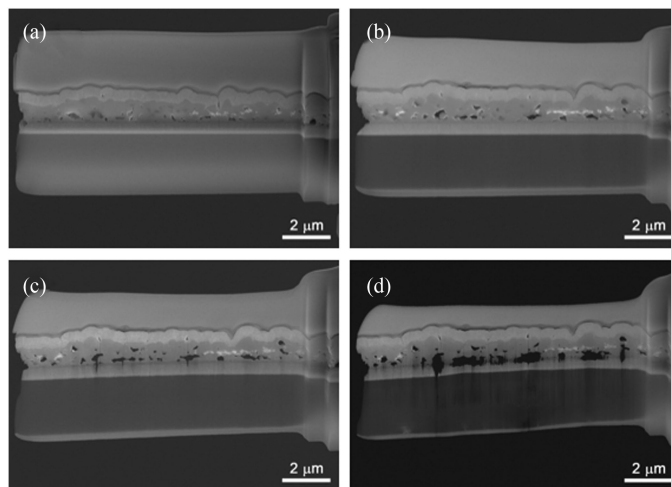


Fig. 4. Evolution of the lamella with the thinning-down process at several acceleration voltage stages. (a) and (b) Evolution during the 30-kV stage, (c) after the 2-kV stage, and (d) the final result after a 1-kV polishing stage.

presence of voids, compared with the STEM images, is significantly reduced. A very small number of what might be voids is present close to the Mo interface. However, contrary to the STEM observations voids are only observed at the grain boundaries of the CZTSe grains. These large CZTSe grains present a dimension similar to the film thickness. Additionally, small grains around the middle of the film with a brighter contrast can be seen. The contrast difference suggests a different chemical composition in the bright grains. Even though the identification of voids using SEM is much more complex because of the fracture/cleavage process, this basic analysis indicates that the voids observed in the TEM analysis are not present prior to the FIB preparation.

As an additional evidence of the appearance of voids during the lamella preparation, in Fig. 4 we present, four SEM images that show the voids formation during the lamella thinning-down process for a second lamella prepared from the same CZTSe sample. After a 30-kV thinning, some voids are already visible, as shown in Fig. 4(a). As discussed previously, some of these voids could already be present in the film. As the thinning-down process progresses, the images show the appearance of more voids as well as their increase in size even for the stages where a lower acceleration voltage is used [see Fig. 4(b)–(d)].

Additionally, we performed Raman scattering spectroscopy, as by XRD, CZTSe cannot be distinguished from ZnSe. The analysis was performed after a standard 1 minute 5% HCl chemical etch process to remove the ZnO layers and most of the CdS, so that most of the absorber layer could be probed. The Raman spectra taken on the surface [Fig. 5(a)] show peaks at 174, 195, and 233 cm^{-1} corresponding to CZTSe, and at 300 cm^{-1} related to CdS, the latter showing an incomplete etching process of the CdS layer. However, the Raman spectroscopy analysis is only capable of probing down to a few hundred nanometers from the top surface due to the high light absorption coefficient of CZTSe [20], [48]. Hence, we also performed an analysis on the cross section to probe the full thickness. This kind of analysis is quite

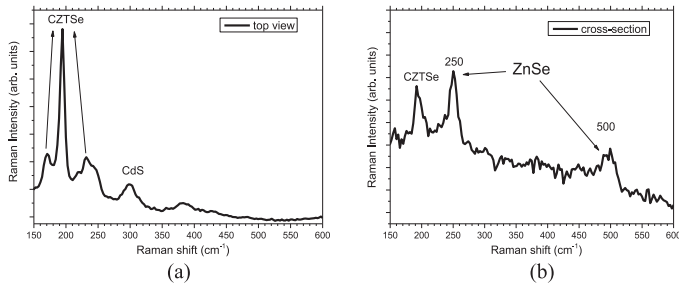


Fig. 5. Raman scattering spectroscopy analysis of the (a) surface and (b) cross section of a CZTSe sample. The surface measurement shows only the presence of CZTSe and CdS, whereas the cross section reveals the appearance of ZnSe.

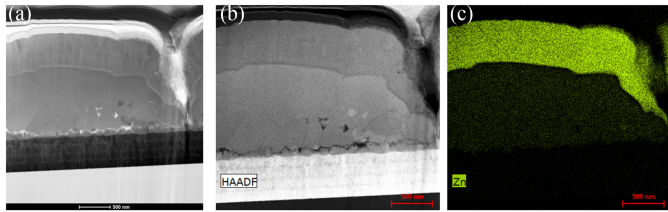


Fig. 6. (a) BF image of the cross section of a CZTSe solar cell with reduced number of secondary phases. (b) HAADF of the same area and (c) EDS mapping of Zn showing no segregation.

complex as the laser spot size is on the same order of magnitude as the film thickness itself, and thus, the volume probed is higher than the effective film volume with a compromise in signal to noise level. The results are shown in Fig. 5(b) confirming the presence of the CZTSe phase, as expected, but now ZnSe is also visible with peaks at 250 and 500 cm^{-1} [20]. The conjugation of both measurements allows us to conclude that ZnSe is present in the depth of the CZTSe film but not at the film's surface. Thus, the Raman spectroscopy analysis supports the EDS interpretation that the CZTSe sample has ZnSe segregates. It is also important to note that neither voids seen by the STEM nor ZnSe phases seen by Raman spectroscopy were identified at the surface of the sample. Hence, this is a further indication that the voids and the ZnSe segregates might be related.

To validate if the appearance of the voids could be related with Zn-rich segregates, a lamella of a second CZTSe solar cell fabricated with optimized conditions that minimize the appearance of secondary phases was prepared by FIB following the same protocol and analyzed similarly [49]. For this optimized fabrication process, the amount of secondary phases is smaller [49]. In Fig. 6, the BF image of the cross section is presented and, compared with the previous sample, the number of observable voids is dramatically reduced. The HAADF image confirms this observation. EDS mapping of Zn, shown in Fig. 6(c), shows no segregation. Hence, when there is a reduced number of ZnSe segregates, there is also a reduced number of voids in the TEM lamella.

Having demonstrated a correlation between the ZnSe aggregates in the EDS analysis close to the voids and the presence of ZnSe secondary phases in the bulk of the CZTSe absorber, we now provide for an explanation why the voids appear during the FIB lamella preparation. At this point, we note that the presence

TABLE I
AVERAGE NUMBER OF SPUTTERED ATOMS WHEN A Ga ION WITH ENERGY OF 30 AND 1 kV STRIKES A SOLID MIXTURE OF Zn, ZnSe, AND CZTSe

	Compound	Zn	Se	Sn	Cu
Ga ion beam at 30 kV	ZnSe	23.4	15.0	-	-
	CZTSe	6.0	15.6	2.6	5.3
Ga ion beam at 1 kV	ZnSe	3.2	2.0	-	-
	CZTSe	0.8	2.1	0.3	0.8

of ZnSe as a secondary phase is largely reported in the literature as it depends on the growth conditions of the CZTSe layer [50]–[52]. We simulated the sputtering yield of the different elements involved when a 30-kV Ga ion beam is incident at a 3° angle, to simulate the effects of the beam tail, using the *Stopping and Range of Ions in Matter* software. The results are summarized in Table I and, basically, in a solid mixture of Cu–Zn–Sn–Se with ZnSe, an incident Ga^+ beam with an energy of 30 kV sputters away around four times more Zn if it hits ZnSe compared with the same beam hitting CZTSe. Thus, if a compound is constituted by a mixture of CZTSe and ZnSe, a bombardment of Ga^+ ions will sputter away Zn in the ZnSe phase four times more efficiently than Zn in the CZTSe phase. This observation is true both for 30 and 1 kV. It is then evident that during the FIB thinning-down process of the CZTSe lamella, the presence of a ZnSe secondary phase can lead to the appearance of voids as the ZnSe secondary phases are sputtered preferentially. While a realistic simulation of the lamella milling accounting for material re-deposition [53], ion beam tails [54] ion channeling [55], [56] and other [42], [43] issues that can influence the formation of voids is a very complicated task, our simple modeling fits and explains well the observed results. The exact reason why part of the ZnSe aggregates are sputtered away while some minor ZnSe phases stays close to the voids could be explained by a non-three-dimensional (3-D) uniformity of the phase distribution but again, these simulations are complex and it is intuitive to understand that a surface sputtering of a non-uniform 3-D thin film can lead to several effects.

IV. CONCLUSION

In this paper, we identified two different types of voids seen in TEM lamellas. The first type of voids is natural occurring voids that are evenly coated by CdS during the chemical bath deposition and that are present in the early stages of the FIB preparation and in SEM cross-sectional images. These voids are usually attributed to Kirkendall effects [44]–[46]. The second type of voids, larger and present with a higher amount compared with the natural occurring voids, are the likely results of the FIB preparation of CZTSe TEM lamellae. In some cases, preparation of CZTSe thin films by FIB can exhibit preferential loss of ZnSe leading to void formation. Therefore, care needs to be exercised when analyzing composition and void formation mechanisms during processing of the films. The preferential loss of ZnSe is supported by several characterizations performed. First, an increased amount of ZnSe close to the voids was seen by the EDS analysis. Second, cross-sectional images

taken during the thinning-down process clearly show an increase in both size and number of voids in the CZTSe film. Third, the void formation can be explained by simple sputtering simulations that show a preferential sputtering of ZnSe versus CZTSe, with four times higher sputtering efficiency for ZnSe. Finally, a CZTSe sample that was intentionally optimized and prepared with a lower concentration of ZnSe secondary phases shows almost no voids. Hence, the observation of voids in kesterite samples using TEM analysis has to be taken with care if the preparation of the lamellae is done using FIB. In fact, several works found voids and local excess of Zn(S, Se) [57]–[61], which are the main indications of the artifacts found in our study. TEM studies have to be paired with other analysis in order to have complementary data. A suggestion is to document the FIB thinning-down process with SEM images and EDS mapping, a process which, unfortunately, is very elaborate. We note that even for TEM specimen prepared with other means, the artifacts can also appear since most of them also use ion-based polishing steps. We note that the findings of this paper might not be universal for kesterites as many factors influence the sputtering process during the FIB preparation. Specifically, properties that are heavily influenced by the preparation method such as: grain boundaries and orientation; different types of segregations and secondary phases; elemental depth and lateral profiling; pre-existence of other features as voids or differences in density. Hence, only a very complex analysis that would include the sample conditions would allow one to understand the full effect of the FIB sputtering on the sample preparation. However, the use of more advanced preparation techniques with either cryo steps or rocking approaches could also be a solution to the found artifacts.

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Authors' photographs and biographies not available at the time of publication.