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# Secondary phase and Cu substitutional defect dynamics in kesterite solar cells: Impact on optoelectronic properties

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## ABSTRACT

Low open circuit voltage ( $V_{OC}$ ) has been recognized as one of the principle limitations in the current generation of kesterite based solar cells. In order to investigate the origin and possible solution for this problem, the influence of point defects and secondary phases on the performance of  $Cu_2ZnSnSe_4$  (CZTSe) devices is explored. Compositionally graded CZTSe films have been prepared with nearly 200 solar cells, each with minute changes in cation composition. Systematic structural characterization of these absorbers with Raman spectroscopy and X-ray diffraction is used to detect secondary phases and defect clusters, and their relative concentration is correlated to device properties. The presented results show the experimental evidence of the effect of the Cu-substitutional defects, in particular  $[V_{Cu} + Zn_{Cu}]$ , on the optoelectronic properties, especially  $V_{OC}$ . It is shown that  $V_{OC}$  can be tuned by adjusting composition, and consequently the amount of the  $[V_{Cu} + Zn_{Cu}]$  defect clusters. Furthermore, it is proven that this is intrinsic property of the CZTSe material, independent of the synthesis and post-deposition processes used for the preparation of samples. Secondary phases are also found to influence device properties, and their effects are dependent on whether they are present in the bulk or surface of the absorber.

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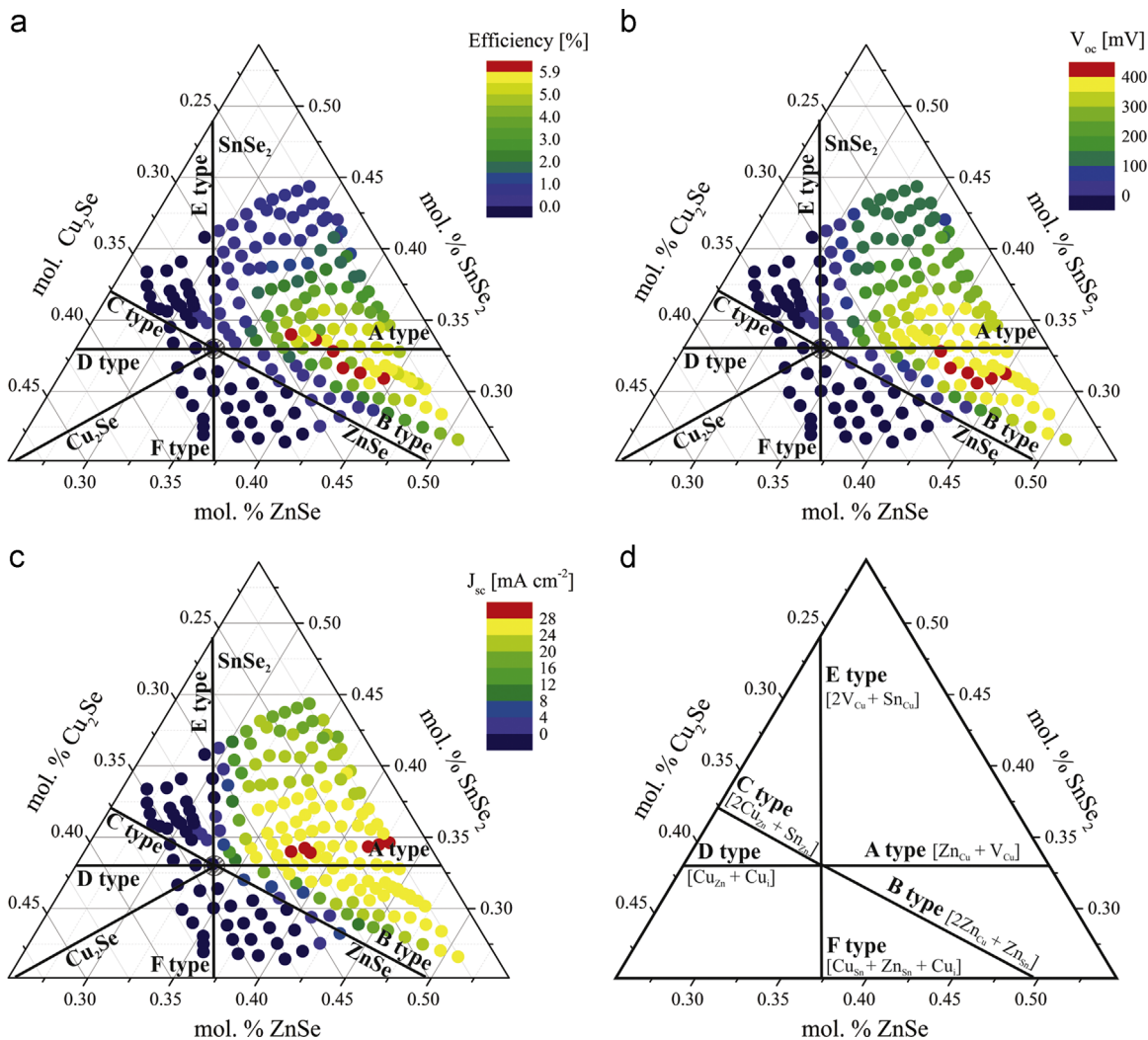
## 1. Introduction

The presence of point defects in a semiconductor material plays a significant, even dominant role in determining its electronic and optical characteristics, and as such, identifying and understanding their influence on material properties is of critical importance. While monoatomic (Si, Ge) and binary (GaAs, SiC, CdTe) semiconductors have relatively simple and well-known defect structures, both intrinsic and extrinsic [1–3], there is a growing number of applications for more complex multinary compounds for which these structures are not well understood. Several multinary compounds are being investigated especially for photovoltaic applications, including chalcopyrites ( $A^+B^3+X_2^{2-}$ ) [4] and the related kesterites ( $A_2^+B^{2+}C^{4+}X_4^{2-}$ ) [5,6], perovskites ( $A^{2+}B^{4+}X_3^{2-}$ ) [7], and mohite ( $A^{2+}B^{4+}X_3^{2-}$ ) [8]. A complicating factor in the application of many of these compounds is the use of off-stoichiometry compositions for the best device performance, which greatly increases the probability of forming secondary phases and point defects.

Kesterite  $Cu_2ZnSnSe_4$  (CZTSe) and its related compounds hold particular interest as light absorbers for solar cells due to being composed of earth-abundant elements, with record efficiencies of 11.6% [9], and even higher (12.6%) for the related  $Cu_2ZnSn(S,Se)_4$  material [10]. The highest performing devices are made from kesterites with Cu-poor ( $Cu/(Zn+Sn) < 1$ ) and Zn-rich ( $Zn/Sn > 1$ ) compositions. Such conditions have been shown both theoretically and experimentally to enhance the formation of Zn(S,Se), while suppressing formation of Cu-(S,Se) and Cu-Sn-(S,Se) secondary phases [11,12]. Regarding defect formation, the more energetically favorable defect clusters have been calculated to be  $[Cu_{Zn} + Zn_{Cu}]$ ,  $[V_{Cu} + Zn_{Cu}]$ ,  $[2Zn_{Cu} + Zn_{Sn}]$ , and  $[2Cu_{Zn} + Sn_{Zn}]$  [13], and the few experimental works on the subject thus far confirm this [14–16]. Aside from their formation, the impact of secondary phases and especially of defects on optoelectronic properties of solar cells is not fully understood. Secondary phases such as binary and ternary Cu-, Zn-, and Sn-sulfides and selenides in the absorbers can reduce the carrier transport and lead to an increased recombination, which in general have detrimental effects on the optoelectronic properties [6]. The influence of point defects is thus far estimated by theoretical studies to affect charge transport properties and modify the band alignment with the n-type buffer layer, which is an important factor in determining the current and voltage which can be extracted from a device [12,13].

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**Fig. 1.** Compositional dependence of device (a) efficiency, (b)  $V_{oc}$  and (c)  $J_{sc}$  shown in a pseudo-ternary phase diagram of  $Cu_2Se$ - $ZnSe$ - $SnSe_2$  for compositionally graded CZTSe solar cells; lines indicate expected secondary phases or defect clusters for a given region. (d) Pseudo-ternary phase diagram of  $Cu_2Se$ - $ZnSe$ - $SnSe_2$  with lines indicating different defect clusters.

In order to closely examine the influence of point defects and secondary phases on the performance of CZTSe-based solar cells, compositionally graded CZTSe films have been prepared with minute changes in cation composition [17]. Approximately 200 solar cells have been fabricated on a single large sample, each with slight differences in absorber composition covering the range of Cu-poor and Zn-rich compositions used in the highest performance CZTSe-based devices, and extending also to stoichiometric, Cu-rich and Sn-rich compositions. Optoelectronic properties are found to rapidly degrade when moving from the Zn-rich cells to the Cu-rich cells, and in a more gradual trend when moving towards the Sn-rich cells. Systematic structural characterization of the absorbers with Raman spectroscopy and X-ray diffraction (XRD) is used to detect secondary phases and defect clusters, and their relative concentration is correlated to device properties. This has been done by the analysis of the changes of the relative intensity of Raman bands that are sensitive to the presence of these defect clusters [16]. Special emphasis is placed on Cu substitutional defects, namely the charge compensated  $[V_{Cu} + Zn_{Cu}]$  cluster, for which a clear effect of the variations in the concentration of this defect cluster on the open circuit voltage ( $V_{oc}$ ) of the devices is observed.

## 2. Materials and methods

Compositionally graded metallic (Cu-Zn-Sn) precursor films were deposited by DC-magnetron sputtering (Alliance Ac450) onto Mo-coated soda-lime glass substrates. During deposition the substrate was not rotated, and due to the positioning of the three off-center targets (Cu, Zn, Sn), a film with gradual lateral composition changes is formed. The precursor films were then subjected to a two-step thermal process in a selenium containing atmosphere to convert it into a CZTSe film, with a composition range of  $Cu/(Zn+Sn)$  from 0.55 to 1.20 and  $Zn/Sn$  from 0.70 to 1.90 [17]. A CZTSe-based device was fabricated by chemical bath deposition of a CdS buffer layer (60 nm), followed immediately by pulsed DC-magnetron sputtering deposition of undoped ZnO (50 nm) and ZnO:Al (450 nm,  $19 \Omega/\square$  sheet resistance) (CT100 Alliance Concepts). More details regarding the deposition of these layers can be found in [11,18]. The device was mechanically scribed into  $3 \times 3 \text{ mm}^2$  cells, forming approximately 200 individual solar cells with gradual changes in composition with respect to neighboring cells. The composition of each cell was measured by x-ray fluorescence spectroscopy (Fischer XVD). AM1.5 illuminated  $J$ - $V$  characteristics (ABET3000 Solar Simulator) and external quantum

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