The nature of electrostatic potential fluctuations in Cu$_2$ZnSnS$_4$ and their role on photovoltaic device performance

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Abstract. Aberration corrected STEM EELS is used to investigate point defects in Cu$_2$ZnSnS$_4$ (CZTS). Nano-scale clusters of Zn$_{Cu}$ anti-site donors are observed with the donor concentration being sufficiently high to degenerately dope the semiconductor. Uncompensated donors and acceptors result in electrostatic potential fluctuations within the material. The effect of these potential fluctuations on the photovoltaic device properties is discussed.

1. Introduction

Cu$_2$ZnSnS$_4$ (CZTS) shows considerable promise as a thin-film photovoltaic absorber layer for Tera-Watt energy production since it has none of the materials issues, such as abundance, toxicity and cost, that are expected to be bottlenecks for CdTe and Cu(In,Ga)Se$_2$ (CIGS) technologies. Despite limited thermodynamic stability of the CZTS phase causing secondary phase precipitation the record cell efficiency for CZTS is at present 11.1% [1]. Defect free CZTS forms in one of two tetragonal crystal structures, named kesterite and stannite after the parent mineralogical phases [2]. Kesterite and stannite can be derived from the chalcopyrite CIGS phase by replacing two group IIIb elements (In/Ga) with a group IIb (Zn) and group IVb element (Sn), thereby satisfying the octet rule; ordering of the Cu and Zn cations within the (004) lattice planes gives rise to the two CZTS polymorphs (figure 1a). Since Cu and Zn are neighbouring elements in the periodic table, the changes in bonding are subtle, with the result that the theoretical energy difference between the two structures is only 3 meV/atom [3]; this allows for Cu, Zn cation intermixing as confirmed by neutron diffraction [4]. Uncompensated point defects give rise to electrostatic potential fluctuations within the material as well as energy states within the band-gap which are Shockley-Read-Hall (SRH) recombination sites. Indeed Romero et al. [5] observed a blue shift of the main CZTS luminescence peak during carrier injection, either by increased temperature or illumination intensity, and attributed this to a transition from band tail recombination to band-band recombination at the high carrier densities where the amplitudes of the potential fluctuations are diminished. Density functional theory studies for CZTS [6] shows Cu$_{Zn}$V$_{Cu}$ to be acceptors with low formation energy while Zn$_{Cu}$ is a low formation energy donor. Point defects associated with the multi-valent Sn ion on the other hand tend to have energy levels deep within the band-gap [6,7].
In this contribution, aberration-corrected, analytical scanning transmission electron microscopy (STEM) is used to identify point defects in CZTS. Structural information is extracted at the nano-scale that complements results from neutron diffraction [4], a technique that requires much larger sample volumes. The experimental results have been reported previously [8] and will therefore be only summarised here for completeness. This precedes a detailed discussion on the role of potential fluctuations on photovoltaic device properties. The discussion is a synthesis of extensive literature results for grain boundary potential fluctuations [9,10] as well as potential/band-gap fluctuations due to composition inhomogeneities in CIGS [11,12].

2. Sample and methods

Bulk CZTS samples were synthesised by annealing elemental powders at 800 °C for 24 hours, the starting composition of the weighed material being Cu$_{1.5}$ZnSnS$_4$ (i.e. Cu-poor). Sulphur was placed separately to the other elements in an evacuated quartz ampoule during annealing. The crushed powder was dispersed onto a holey carbon grid and analysed using an aberration corrected Nion UltraSTEM operating at 100 kV. The composition was measured using electron energy loss spectroscopy (EELS); probe convergence and EELS semi-collection angles were 31 mrad.

3. Results and Discussion

3.1 Aberration corrected STEM EELS

Figure 1(a) is a schematic of the kesterite and stannite crystal structures. As mentioned previously, the two phases differ in the ordering of Cu and Zn cations within the (004) planes. Viewing the tetragonal crystal along the $a$-axis we find the pure Sn atom columns to be separated by three atom columns of either pure Cu or pure Zn in a direction parallel to the $c$-axis. Sn appears brighter in a STEM high angle annular dark field (HAADF) image due to its larger atomic number and therefore provides unique reference points of the atoms within the unit cell. Chemical analysis of the three Cu/Zn atomic columns sandwiched between the Sn columns within the unit cell is sufficient to distinguish between pure kesterite and stannite phases. For the former the composition of the atom columns varies as Cu, Cu, Zn (or its reverse), while in the latter the variation is as Cu, Zn, Cu. An atom column containing both Cu and Zn shows evidence for Cu, Zn disorder within the unit cell (i.e. either Zn$_{Cu}$ or Cu$_{Zn}$ anti-site atoms).

Figure 1(b) is a HAADF image of CZTS in the $a$-axis orientation. Cu and Zn L-edge EELS spectra for the probe positioned on atom columns labelled atom1, atom2 and atom3 were extracted from a line spectrum image acquired along the direction marked by the arrow (these atom columns are sandwiched between the Sn columns labelled Sn1 and Sn2). The individual EELS spectra are shown superimposed in figure 1(c). The shape of the EELS spectra is similar for all three atom columns and reveals the Zn L-edge clearly but little or no intensity for the Cu L-edge at ~930 eV. Since for both kesterite and stannite two atom columns must be pure Cu this implies the presence of a large concentration of Zn$_{Cu}$ donor anti-site atoms. There is evidence for the measurement being influenced by electron beam broadening within the sample, since the EELS signal extracted from a Sn column (e.g. Sn1) shows a similar spectrum shape to that in figure 1(c), despite no (or very little) Zn being expected within the Sn column. The geometric spreading of the electron probe is of the order of a few nanometres, suggesting that the composition inhomogeneity observed is a particularly large point defect cluster. If it is assumed that all Cu atoms in the unit cell are replaced by Zn (i.e. no Cu vacancies) the Zn$_{Cu}$ donor concentration is estimated to be $\sim 10^{22}$ cm$^{-3}$. This is considerably larger than typical values for the effective density of states in the conduction band so that the material is degenerately doped locally. It should be mentioned however that most STEM EELS measurements revealed atom columns with mixed Cu, Zn compositions, although beam spreading is always present as in figure 1. Further details of the STEM EELS results can be found in [8].
3.2 Band structure of a point defect cluster

A schematic band structure of the experimentally determined point defect cluster is shown in figure 2a. The Zn\(\text{Cu}\) anti-site atoms are assumed to be ionised, with the result that positive charge is accumulated over the cluster of size \(d\). The increase in potential leads to downward bending of the conduction and valence bands. The point defect cluster therefore acts as a sink for electrons and barrier for holes; consequently it is less \(p\)-doped than the neighbouring bulk (\(p\)-type) CZTS. Minority electrons within CZTS screen the positive charge of the cluster over a distance governed by the Debye screening length. Zn\(\text{Cu}\) anti-site atoms are shallow donors [6] but, due to degenerate doping, the discrete energy level is broadened into a continuous band that extends into the conduction band. Note that the band structure for the point defect cluster has features similar to charged grain boundaries [9,10].

In the above analysis any change in lattice parameter due to Zn\(\text{Cu}\) anti-site atoms has not been taken into account. Strain gives rise to band-gap fluctuations superimposed on to the electrostatic potential band bending. In CIGS, the band-gap depends on the Ga content, so that band-gap fluctuations can also be generated by variations of the Ga/(In+Ga) ratio. Similar effects may occur in CZTS as well. For example, the highest performing CZTS devices have mixed S and Se anions [1,2], with Se-rich compositions giving smaller band gaps compared to S-rich compositions.

3.3 Effect of electrostatic potential fluctuations on device performance

The donor/acceptor energy level of an electrostatic potential fluctuation is a SRH recombination site and can therefore affect photovoltaic device parameters. SRH recombination is largest when (i) the electron and hole concentrations at the defect are equal and (ii) the defect energy level lies deep within the band-gap. Figures 2(b) and 2(c) are band structure diagrams for single energy level uncompensated donors and acceptors, respectively. The first criterion for SRH recombination means that in \(p\)-type CZTS uncompensated donors are stronger recombination sites than uncompensated acceptors (the latter is a sink for majority carrier holes so that the cluster region is more \(p\)-doped than the neighbouring CZTS). The requirement of deep defect levels means that point defects of Sn are more likely to be deleterious than (say) shallow Zn\(\text{Cu}\) anti-site atoms. Furthermore, electrical bias also has an important effect on SRH recombination. On biasing, the electron and hole quasi-Fermi levels move towards the conduction and valence band respectively, such that their separation is proportional to the applied voltage. Under high injection conditions the potential change (i.e. band bending) at the cluster

**Figure 1:** (a) crystal structure of kesterite and stannite, (b) STEM HAADF image of CZTS along the \(a\)-axis and (c) EELS spectra for the probe positioned on the indicated atom columns.

**Figure 2:** Schematic band structure diagrams for (a) Zn\(\text{Cu}\) cluster observed experimentally, (b) single energy level uncompensated donors and (c) single energy level uncompensated acceptors.
will also diminish, in a manner similar to grain boundaries [9], due to changes in the defect level occupancies. The comparable electron and hole populations result in stronger recombination under bias for both uncompensated donors and acceptors.

On a macroscopic level the device $J-V$ characteristics can be described as:

$$J(V) = [J_{\text{diode}}(V) + J_{\text{SRH}}(V)] - J_{\text{SC}}$$

(1)

where $J_{\text{diode}}$ is the current due to radiative recombination, $J_{\text{SRH}}$ the current due to SRH recombination within the space charge region and $J_{\text{SC}}$ is the photogenerated short circuit current. From previous studies on grain boundaries [10], point defect clusters are not expected to significantly affect $J_{\text{SC}}$; this is because materials such as CZTS absorb most of the light near the space charge region, so that only carriers generated from long wavelength photons are likely to be lost to recombination in the diode quasi-neutral region. Furthermore, for high efficiency cells, the fraction of defect-free regions is still high enough for generating a large $J_{\text{SC}}$. On the other hand, recombination at point defect clusters in the space charge region will increase $J_{\text{SRH}}$ so that the open circuit voltage ($V_{\text{OC}}$) is reduced. The higher diode ideality factor for $J_{\text{SRH}}$ also leads to a reduction of the fill factor. The decrease in $V_{\text{OC}}$ can be offset via a series resistance [12], so that the voltage across the point defect cluster is lowered, thereby reducing SRH recombination rates. The series resistance can be due to point defect clusters which are obstacles to majority carrier flow, i.e. uncompensated donors within the quasi-neutral diode region (figure 2b), or as a more extreme example, current blocking secondary phases such as ZnSe [13]. Nevertheless, the series resistance also deteriorates the fill factor so that an optimum series resistance exists where the two effects are balanced [12]. Finally, any band-gap fluctuations will affect $J_{\text{diode}}$ as this is governed by radiative recombination; a decrease in band-gap tends to equalise electron and hole populations resulting in a larger $J_{\text{diode}}$ and hence smaller $V_{\text{OC}}$.

4. Conclusions

Aberration corrected STEM EELS has provided the first direct evidence for electrostatic fluctuations in CZTS in the form of a nano-scale Zn$_{\text{Cu}}$ donor anti-site atom cluster that is degenerately doped. Reference to the literature indicates that such point defect clusters are expected to be a site for Shockley-Read-Hall recombination, with the result that the open circuit voltage and fill factor are reduced simultaneously. Uncompensated donors in p-type material are stronger recombination centres than uncompensated acceptors. Furthermore an optimised series resistance can be beneficial in minimising the deleterious effects of point defect cluster recombination.

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