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Defect levels in Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ solar cells probed by current-mode deep level transient spectroscopy

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Defect levels in kesterite Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) solar cells have been investigated by current-mode deep level transient spectroscopy. Experiments were carried out on two CZTSSe cells with photoconversion efficiencies of 4.1% and 7.1% measured under AM 1.5 illumination. The absorber layer of the 4.1% efficiency cell was prepared by annealing evaporated ZnS/Cu/Sn stacked precursor under S/Se vapor, while the absorber of the 7.1% efficiency cell was prepared by co-evaporation of the constituent elements. The 4.1% efficiency CZTSSe cell with a S/(S + Se) ratio of 0.58 exhibited two dominant deep acceptor levels at $E_a = 0.12$ eV, and $E_a = 0.32$ eV identified as CuZn(-/-) and CuSn(-/-) antisite defects, respectively. The 7.1% efficiency cell with purely Se composition $S/(S + Se) = 0$ showed only one shallow level at $E_c + 0.03$ eV corresponding to Cu-vacancy ($V_{Cu}$). Our results revealed that $V_{Cu}$ is the primary defect center in the high-efficiency kesterite solar cell in contrast to the detrimental CuZn and CuSn antisites found in the low efficiency CZTSSe cells limiting the device performance. © 2014 AIP Publishing LLC.

Copper-based I$_2$-II-IV-VI$_4$ quaternary kesterites—Cu$_2$ZnSnS$_4$ (CZTS), Cu$_2$ZnSnSe$_4$ (CZTSe), and mixed chalcogen Cu$_x$Zn$_{1-x}$Sn$_y$S$_{1-y}$ (CZTSSe) have recently emerged as the most promising absorber material system alternative to CuIn$_3$Ga$_{1-x}$Se$_2$ and CdTe absorbers in thin-film solar cells which comprise of scarce, highly expensive, and toxic elements. With a tunable direct bandgap of 1.0–1.5 eV and a large absorption coefficient ($\alpha > 10^6$ cm$^{-1}$), the Shockley-Queisser photon balance calculations predict the theoretical efficiency limit for a single junction CZTSSe solar cell to be as high as 32.2%. One of the major factors restricting the efficiency of polycrystalline thin-film solar cells is the presence of deep-lying electronic trap levels in the bulk of the absorber layer and interfacial states localized at the heterojunction hindering the charge transport. Kesterite solar cells are far more vulnerable to have large number of such defects in the absorber film compared to the chalcopyrites as the stability of single phase stoichiometric CZTSSe could only be found at a much narrower region in the three-dimensional ($\mu_{Cu}$, $\mu_{Zn}$, $\mu_{Sn}$) chemical potential space and the Cu$_2$(S,Se)-Zn(S,Se)-Sn(S,Se)$_2$ ternary phase diagram. Theoretical studies based on density functional theory first-principle calculations have predicted intrinsic point defects including vacancies ($V_{Cu}$, $V_{Zn}$, $V_{Sn}$, and $V_{S}$), antisites (Cu$_{Zn}$, Zn$_{Cu}$, Cu$_{Sn}$, Sn$_{Cu}$, Zn$_{Sn}$, and Sn$_{Zn}$), interstitials (Cu$_i$, Zn$_i$, and Sn$_i$), and several defect complexes (e.g., [Cu$_{Zn}$ + Zn$_{Cu}$], [V$_{Cu}$ + Zn$_{Cu}$], etc.) that may exist in CZTSSe depending on its composition. However, there exists meagre information on the experimental identification of such electrically active defects in CZTSSe solar cells. In this Letter, we report on the investigation of the deep levels in CZTSSe solar cells probed by current-mode deep level transient spectroscopy (I-DLTS) to quantify the trap activation energies ($E_T$), trap concentrations ($N_T$), and capture cross-sections of the traps ($\sigma_T$).

The conventional capacitive DLTS (C-DLTS) technique is a very sensitive tool to identify electrically active defects in semiconductors in terms of activation energy, defect type, and trap concentration and have been widely used for deep and shallow level defect characterization of chalcopyrites and chalcoledones. The CZTSSe cells under investigation exhibited large depletion capacitance ($C_d$) beyond the detection limit of our DLTS system and therefore we have used I-DLTS technique which uses current transient measurements to identify the defect levels. Although, unlike C-DLTS, I-DLTS cannot distinguish between a majority and minority carrier trap, but it provides valuable information relating to the defect activation energies, defect concentration, and the capture cross-sections of the defect centers.

We have performed I-DLTS measurements on two different Cu$_2$ZnSn(S$_x$Se$_{1-x}$)$_4$ cells in this study, namely, Cell 1 and Cell 2, with Cell 1 having a S/Se ratio of 1.4 ($x = S/(S + Se) = 0.58$), and Cell 2 containing purely Se ($x = 0$). The absorber layer of Cell 1 was prepared by a two-step process: deposition of ZnS/Cu/Sn precursor stacked layer on Mo-coated soda lime glass (SLG) substrates by sequential thermal evaporation followed by annealing under S + Se vapor in a tube furnace. The pure CZTSe absorber of Cell 2 was prepared by co-evaporation of the constituent elements. The finished CZTSSe solar cells had a SLG/Mo/CZTSSe/n-CdS/i-ZnO/Al:ZnO/Al device structure. The J-V characteristics of the two cells under dark and under simulated AM 1.5 illumination are shown in Fig. 1. Cell 1 showed a higher open-circuit voltage ($V_{OC}$) of 506 mV compared to Cell 2, which exhibited a maximum $V_{OC} = 350$ mV at 297 K. Both cells were...
Cu-poor in composition and had a slightly Zn-rich stoichiometry. The compositional details, thickness and bandgaps of the absorber layers for the two cells are listed in Table I. The photovoltaic and electrical parameters of the two cells under investigation are summarized in Table II.

A SULA DDS-12 DLTS system was operated in current transient spectroscopy (CTS) mode to obtain the I-DLTS spectra. Schematic of the experimental set-up is represented in Fig. 2. The samples were mounted on a JANIS VPF800 cryostat stage controlled by a Lakeshore 335 temperature controller. The cells were reverse biased at $V_R = -0.4 \text{ V}$ and a trap filling forward pulse of amplitude $V_a = +0.3 \text{ V}$ with 10 ms pulse width was applied following which the current transients were recorded. The transient signals were successively processed by the CTS unit and the I-DLTS spectra were generated by choosing a suitable rate window using the correlator units to calculate the emission rates at different temperatures following the standard double boxcar method. The correlator unit in DDS-12 is capable of assigning multiple rate windows in a single thermal scan. From Eq. (1) given below,\textsuperscript{24} it can be seen that the expression of the current transient in I-DLTS also contains the steady-state diode leakage current

$$i(t) = \frac{qWA}{2\tau_{e,h}}N_T(t) + I_L,$$

where $q$ is the electronic charge, $W$ is the width of the measurement volume, $A$ is the diode area, $\tau_{e,h}$ is the decay constant for the current transients corresponding to electron or hole emissions, and $N_T$ is the concentration of trapped charge carriers. If the diode leakage current exceeds a certain limit it can obscure the current transients. The correlator unit also removes the background leakage current prior to the measurements to avoid any such issues. The current transient captures were time delayed after the end of each filling pulse by an amount called the initial delay. The rate windows $\tau$ for the transient capture are dependent on the initial delays in the following way

$$\tau = \frac{1}{(1.94 \times \text{initial delay (ms)})}.$$

The capture cross-sections and the trap concentration were calculated from the I-DLTS plots. The activation energies ($E_T$) of the deep centers were extracted from the Arrhenius plots obtained from the emission rates calculated from the current transients.

The I-DLTS scans of Cell 1 and Cell 2 in the temperature range of 85–325 K are shown in Figs. 3(a) and 3(b), respectively. It can be readily observed that the defect characteristics in these two cells are quite different. For Cell 1, two broad peaks were noticed, one close to 190 K (peak 1) and the other one close to 285 K (peak 2) for the lowest initial delay of 0.1 ms. Such broad peaks signify a slow emission rate of the defect centers. Interestingly, none of these two peaks were observed in Cell 2, rather a new peak (peak 3) appeared close to 100 K (for an initial delay of 0.02 ms) which is much narrower signifying a faster emission of trapped carriers from the associated defect center.

The Arrhenius plots corresponding to the observed peaks in the I-DLTS scan are shown in Fig. 4. Activation energies of $E_{T1} = 0.12 \text{ eV}$ and $E_{T2} = 0.32 \text{ eV}$ were extracted corresponding to peaks 1 and 2, respectively. Due to the broad distribution of the emission rates, the uncertainties in the activation energies in Cell 1 were estimated to be $\pm 0.04$ for $E_{T1}$ and $\pm 0.06 \text{ eV}$ for $E_{T2}$. An activation energy of $E_{T3} = 0.03 \pm 0.01 \text{ eV}$ was calculated corresponding to the peak 3 in Cell 2.

Recent theoretical analysis of defect models in kesterite CZTS and CZTSe materials\textsuperscript{10,15–20} have been considered to assign the experimentally observed defect levels in this study. Nagoya et al.,\textsuperscript{15} Maeda et al.,\textsuperscript{16,17} and Chen and co-workers\textsuperscript{10,18–20} have carried out systematic theoretical studies on the intrinsic point defects in CZTS/CZTSe and calculated the formation energies and corresponding transition (activation) energies for various point defects. It is predicted that the acceptor defects (Cu$\text{Zn}$, V$\text{Cu}$, Zn$\text{Sn}$, V$\text{Zn}$, Cu$\text{Se}$, etc.) have much lower energy of formation compared to the donor.

<table>
<thead>
<tr>
<th>Cell ID</th>
<th>Area (cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>Efficiency, $\eta$ (%)</th>
<th>Ideality factor, $n$</th>
<th>Series resistance (Ω)</th>
<th>Shunt resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 1</td>
<td>0.42</td>
<td>506</td>
<td>22.5</td>
<td>35</td>
<td>4.1</td>
<td>4.5</td>
<td>31.2</td>
<td>125</td>
</tr>
<tr>
<td>Cell 2</td>
<td>0.43</td>
<td>350</td>
<td>32.7</td>
<td>62</td>
<td>7.1</td>
<td>1.4</td>
<td>5.06</td>
<td>357</td>
</tr>
</tbody>
</table>

The photovoltaic and electrical parameters of the two cells are given below

![Image](image-url)
defects in these material systems for Cu-poor composition. The CuZn antisite defect has the lowest formation energy which acts as an acceptor level located about 0.10–0.15 eV above the valence band maxima (VBM) and is considered to be responsible for the intrinsic p-type conductivity of these materials. The copper vacancy (VCu) has comparatively higher energy of formation than CuZn antisite and contributes to a much shallower acceptor level at ~0.02 eV above the VBM. It is suggested that VCu is much preferable than the CuZn antisite for high performance solar cells, since CuZn produces deeper acceptor level than VCu and is thus detrimental to the cell performance. Existence of CuZn deep level at En + 0.12 eV has also been experimentally identified by admittance spectroscopy.

The theoretical studies strongly suggest that the observed trap level ET1 in Cell 1 with an activation energy of 0.12 eV can be assigned to the CuZn(-/0) antisite defect. The second dominant defect level identified in Cell 1 (ET2) corresponds to a much deeper level with an activation energy of 0.32 eV which matches closely to the transition energy theoretically calculated for CuSn (2-/-) defect. The larger capture cross-section of ET2 compared to that of ET1 also suggests that ET2 has a more negatively charged state. Therefore, we attribute the deep level at En + 0.32 eV to the CuSn (2-/-) antisite defect.

In Cell 2, the activation energy of trap level ET3 = 0.03 eV can be assigned to the copper vacancy (VCu), as no other shallow level in this range exists in these materials. The experimentally identified value of En + 0.03 eV is in good agreement with the theoretical predicted value of 0.02 eV. All the experimentally identified defect parameters including the defect activation energy (ET), capture cross-section (σT), trap concentration (Np), and the associated point defects are summarized in Table III.

We would like to emphasize that a device having shallow defect levels is expected to exhibit superior performance than a device with deeper defect levels. Our results follow this trend with Cell 2 showing much better photovoltaic efficiency compared to Cell 1.

**TABLE III. Summary of the observed defect levels in the CZTSSe solar cells by I-DLTS.**

<table>
<thead>
<tr>
<th>Cell ID</th>
<th>Peak ID</th>
<th>Approx. peak temperature (K)</th>
<th>Activation energy, ET (eV)</th>
<th>Capture cross section, σT (cm²)</th>
<th>Trap conc. Np (cm⁻³)</th>
<th>Possible defect level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 1</td>
<td>Peak 1</td>
<td>190</td>
<td>0.12 ± 0.04</td>
<td>1.31 × 10⁻²⁰</td>
<td>6.17 × 10¹⁴</td>
<td>CuZn</td>
</tr>
<tr>
<td></td>
<td>Peak 2</td>
<td>285</td>
<td>0.32 ± 0.06</td>
<td>2.04 × 10⁻¹⁸</td>
<td>6.73 × 10¹⁵</td>
<td>CuSn</td>
</tr>
<tr>
<td>Cell 2</td>
<td>Peak 3</td>
<td>100</td>
<td>0.03 ± 0.01</td>
<td>2.52 × 10⁻²⁰</td>
<td>6.46 × 10¹⁵</td>
<td>VCu</td>
</tr>
</tbody>
</table>
performance compared to Cell 1. However, the most interesting observation in this study is the presence of shallow \( V_{Cu} \) level in purely Se containing CZTSe sample (Cell 2) which suggests that although \( CuZn \) has a lower formation energy, it is possible to have \( V_{Cu} \) as the predominant lattice defect in kesterites. Our results also indicate that the intrinsic p-type conductivity of high-efficiency CZTSSe absorbers could be due to the formation of copper vacancies (\( V_{Cu} \)) similar to chalcopyrites and the formation of detrimental \( CuZn \) antisites can be avoided.

In conclusion, we have performed current DLTS measurements on two Cu-poor and Zn-rich CZTSSe solar cells with different chalcogen ratios to probe electrically active intrinsic point defects. The lower efficiency CZTSSe cell (S/Se = 1.4) showed two dominant deep acceptor levels at \( E_v + 0.12 \) eV and \( E_v + 0.32 \) eV corresponding to \( CuZn \) and \( CuSn \) antisites, whereas the pure CZTSe (S/Se = 0) higher efficiency cell showed only a shallow \( V_{Cu} \) level at \( E_v + 0.03 \) eV. Our investigation suggests that \( V_{Cu} \) could be the predominant lattice defect in high efficiency kesterite cells instead of the detrimental \( CuZn \) antisites.

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