Effect of Zn(O,S) Buffer Layer on Cu$_2$ZnSnS$_4$ Solar Cell Performance from Numerical Simulation

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Abstract

Zn(O,S) is a promising alternative buffer layer to CdS in Cu$_2$ZnSnS$_4$ (CZTS) based solar cell due to its large bandgap and nontoxic elements. In this study the performance of CZTS/Zn(O,S)/Al:ZnO solar cell was numerically simulated by Solar Cell Capacitance Simulator (SCAPS). And the sulfur content of Zn(O,S) buffer layer was varied to investigate how the chemical composition of Zn(O,S) influences the conduction band offsets at absorber/buffer and buffer/window interfaces and then affects the cell performance. It was found that the conduction-band offset (CBO) of the CZTS/Zn(O,S) heterojunction played a significant role in the performance of the solar cell. The electron affinity and bandgap of Zn(O,S) are controlled by the sulfur-to-oxygen ratios, and the resulting offset span is from +0.7 eV in the “spike” direction to -0.1 eV in the “cliff” direction if the electron affinity of CZTS is considered as 4.5 eV. When S/(S+O) atomic ratio of Zn(O,S) is about 0.3, the cell has a high conversion efficiency of 14.90% with CBO of 0.2 eV. The simulation results will provide some important guidelines for fabricating high efficient CZTS solar cells.

Key Words: CZTS, Zn(O,S), SCAPS

1. Introduction

Recently Zn(O,S) thin films have a rapid rise in their utility as buffer layers in solar cells due to their compositional and crystal structure tunability, in addition to being used as phosphor host materials and photocatalysts [1]. Upon varying their composition, the bandgap [2], conduction band offset and conductivity can be precisely tuned. Besides, Zn(O,S) is a non-toxic and earth-abundant material with a large bandgap. Therefore it is a promising candidate for replacing the conventional CdS [3,4] as a buffer layer. The Cu(In,Ga)(S,Se)$_2$ (CIGSSe) solar cell with Zn(O,S) buffer layer has achieved an efficiency of 21.0% [5].

Cu$_2$ZnSnS$_4$ (CZTS) has become an attractive absorber material for new photovoltaic cells lately, because of its naturally abundant and nontoxic elements, suitable bandgap energy of about 1.5 eV and absorption coefficient over $10^4$ cm$^{-1}$ [6]. More and more researchers devote themselves to fabricating environmentally friendly solar cell, and CZTS-based cell with Zn(O,S) buffer layer is an optimal choice, which has a conversion efficiency of 4.6% [7] till now.

Nevertheless, the effects of chemical composition of Zn(O,S) buffer layer on CZTS solar cell performance and the operation mechanism are seldom reported. In this
paper, Zn(O,S) buffer layers with different sulfur contents have been used in CZTS solar cells. The properties of corresponding solar cells are evaluated by solar cell capacitance simulator (SCAPS) [8,9].

2. Numerical Simulation

The SCAPS simulation software used in this work is developed at the Department of electronics and information systems (ELIS) of the University of Gent. SCAPS calculates solution of the basic semiconductor equations given by equation (1)–(3) in one-dimensional and steady-state conditions. These are the Poisson equation (equation (1)) and the continuity equations for electrons and holes together with the appropriate boundary conditions (equations (2)–(3)).

\[
\frac{d^2}{dx^2} \psi(x) = \frac{e}{\varepsilon_o \varepsilon_r} (p(x) - n(x) + N_D - N_A + \rho_p - \rho_n) \tag{1}
\]

\[
\frac{d}{dx} J_p(x) - e \frac{\partial n(x)}{\partial t} - e \frac{\partial \rho_n}{\partial t} = G(x) - R(x) \tag{2}
\]

\[
\frac{d}{dx} J_n(x) + e \frac{\partial p(x)}{\partial t} + e \frac{\partial \rho_p}{\partial t} = G(x) - R(x) \tag{3}
\]

where \(\psi\) is electrostatic potential, \(e\) is electrical charge, \(\varepsilon_r\) is relative permittivity and \(\varepsilon_o\) is the vacuum permittivity, \(p\) and \(n\) are hole and electron concentrations, \(N_D\) is charged impurities of donor and \(N_A\) is that of acceptor type, \(\rho_p\) and \(\rho_n\) are holes and electrons distribution, respectively. \(J_p\) and \(J_n\) are electron and hole current densities, \(G(x)\) and \(R(x)\) are charge generation and recombination rates [10,11]. This is a program to simulate the dc and ac electrical characteristics of thin film heterojunction solar cells [12].

In this paper, the CZTS thin film solar cell with the structure of CZTS/Zn(O,S)/Al:ZnO (AZO) is implemented in the SCAPS 3.3 environment. CZTS, Zn(O,S) and AZO are used as absorber, buffer and window layers respectively. The schematic structure of the cell is shown in Figure 1.

The basic input parameters used in the simulation, which are adopted from literature values, theories, or reasonable estimates in some cases, are listed in Tables 1 and 2. The default illumination spectrum is set to the global AM1.5 standard.

3. Band Alignment

The band diagram of the cell is shown in Figure 2. The CBOs at absorber/buffer and buffer/window interfaces are defined as \(\Delta E_{c,ab}^e = \chi_b - \chi_a = E_{cb} - E_{ca}\) and \(\Delta E_{c,w}^e = \chi_w - \chi_a = E_{cw} - E_{ca}\), where \(\chi_a\), \(\chi_b\) and \(\chi_w\) are the electron affinities of absorber, buffer and window layers respectively. \(\phi_h^a\) is the energy barrier from the absorber to the window conduction band (CB) measured from electron quasi-Fermi level. A positive offset is often referred to as a “spike” (as \(\Delta E_{c,ab}^e\) in Figure 2), and a negative one as a

![Figure 1. Structure of CZTS solar cell.](image)

<table>
<thead>
<tr>
<th>Table 1. Device parameters used in simulation</th>
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</thead>
<tbody>
<tr>
<td><strong>Cell properties</strong></td>
</tr>
<tr>
<td>Cell temperature</td>
</tr>
<tr>
<td>Series resistance, (R_s)</td>
</tr>
<tr>
<td>Shunt resistance, (R_{sh})</td>
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<tr>
<td><strong>Back metal contact properties</strong></td>
</tr>
<tr>
<td>Electron work function of Mo</td>
</tr>
<tr>
<td>SRV(^a) of electron</td>
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<tr>
<td>SRV of hole</td>
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<tr>
<td>SRV of hole</td>
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</tbody>
</table>

\(^a\) SRV represents surface recombination velocity.
“cliff” (as $\Delta E_{\text{cb}}^\text{bw}$ in Figure 2). When CBO is positive, a charge carrier has to spend kinetic energy in order to overcome an energy barrier from the small gap to the large gap semiconductor. Vice versa, a carrier gains kinetic energy at a negative offset, but a negative CBO is heavily dependent on the amount of interfacial recombination.

4. Band Variations

Figure 3 shows the band variations of Zn(O,S) based on values determined by various groups [16]. The bandgap variation of Zn(O,S) with S/(S+O) ratio $x$ is approximately

$$E_{\text{ZnS}}^0(x) = xE_{\text{ZnS}}^0 + (1 - x)E_{\text{ZnO}}^0 - b(1 - x)x$$  \hspace{1cm} (4)$$

where $E_{\text{ZnS}}$ and $E_{\text{ZnO}}$ are the bandgaps of ZnS and ZnO (3.6 and 3.2 eV, respectively) and $b$ is the optical bowing parameter of approximately 3.1 eV [20]. The bandgap is minimum when $x$ is about 0.5, and it increases with either a higher or lower S/(S+O) ratio. It can be seen that the sulfur content mainly affects the states of valence band maximum (VBM) for the low values of $x$ and conduction band minimum (CBM) for the high sulfur content.

5. Results and Discussion

5.1 Impacts of Low Sulfur Content of Zn(O,S)

When the ratio of S/(S+O) is lower than 0.5, the

![Figure 2. Band diagram of the heterojunction when applied a bias voltage of V.](image)

![Figure 3. Bandgap energy of Zn(O,S) as a function of S/(S+O).](image)
CBM of Zn(O,S) varies less compared to the change of VBM and thus the electron affinity can be treated as a constant approximately. While \( x \) is between 0 and 0.5, the energy band is in the range of 2.6–3.2 eV, which can be calculated from formula (4). The cell band diagram is shown in Figure 4. Keeping the electron affinity of Zn(O,S) at 4.6 eV, which is the same value of ZnO, the band energy of Zn(O,S) is varied from 2.6 to 3.2 eV. The CBO at CZTS/Zn(O,S) interface keeps -0.1 eV. Figure 5 shows the effects of the bandgap of Zn(O,S) on the cell performance parameters, such as open circuit voltage (\( V_{oc} \)), short circuit current density (\( J_{sc} \)), fill factor (\( FF \)) and efficiency (\( \eta \)). It seems all the cell performance parameters decrease with increasing Zn(O,S) bandgap. However, the amplitude of variation for each parameter is small. It suggests when \( x \) is in the range of 0–0.5, the cell properties do not vary obviously.

### 5.2 Impacts of High Sulfur Content of Zn(O,S)

When \( x \) is higher than 0.5, the VBM of Zn(O,S) varies less compared to the change of CBM and thus the variation of electron affinity almost equals to that of bandgap. In this case the band diagram is shown in Figure 6. It suggests that the CBOs at CZTS/Zn(O,S) and Zn(O,S)/AZO interfaces vary at the same time. When \( x \) is changed between 0.5 and 1, the reported electron affinities are in the range of 3.9–4.6 eV. The corresponding variation ranges of \( \Delta E_{cb}^{ab} \) and \( \Delta E_{cb}^{bw} \) are from 0.6 to -0.1 eV and -0.7 to 0 eV, respectively. The effects of \( \Delta E_{cb}^{ab} \) and \( \Delta E_{cb}^{bw} \) on solar cell performance are shown in Figure 7.

It can be seen from Figure 7 that the efficiency of the cell is mainly controlled by the \( FF \), while \( V_{oc} \) and \( J_{sc} \) show only minor variations with \( \Delta E_{cb}^{ab} \) and \( \Delta E_{cb}^{bw} \).
As $\Delta E_{c \text{bw}}$ is decreased from -0.5 to -0.7 eV and $\Delta E_{c \text{ab}}$ keeps constant, the efficiency decreases, which is mainly due to the lower $FF$. That is, $\phi_n^+$ is the factor limiting the cell performance, because $\Delta E_{c \text{bw}} > 0$ causes the conduction band in the buffer to move up, as shown in Figure 8(a). More and more photo-generated electrons are hindered from leaving the absorber as $\phi_n^+$ increases [21]. When $q\phi_n^+$ overcomes $E_C$ in the absorber, the number of electrons collected by the cathode drops, and so do the current, the $FF$ and the efficiency, as a result, the current density-voltage characteristics start deviating from the standard one. However, when $\Delta E_{c \text{bw}}$ is between 0 and -0.5 eV, the curves have almost the same tendency. That is if $\Delta E_{c \text{bw}}$ is in the range of -0.1–0.4 eV, the cell properties show little change, and when $\Delta E_{c \text{bw}}$ is changed between 0.1 and 0.3 eV, the cell has better performance. With $\Delta E_{c \text{bw}}$ increases from 0.4 to 0.6 eV, $FF$, $J_{\text{sc}}$ and $\eta$ decrease, which can be attributed to the increase of $\phi_n^+$ resulting in the enhancement of the barrier for the electrons in the absorber (as shown in Figure 8(b)).

5.3 Current Density-Voltage Curves

For Zn(O,S) buffer layer used in CIGS solar cell, better cell performance could be achieved with sulfur content of 0.25–0.40. Three different S/(S+O) values were considered to simulate CZTS/Zn(O,S)/AZO properties. The simulation parameters are listed in Tables 1 and 2. The calculated current density-voltage ($J-V$) curves are shown in Figure 9. And the performance of the cells

![Figure 8](image.png)

**Figure 8.** Conduction band energy $E_C$ at (a) $\Delta E_{c \text{bw}} = 0.2$ eV and $\Delta E_{c \text{bw}} = -0.7$ eV (dashed line), -0.5 eV (dotted line), and 0 eV (solid line) and (b) $\Delta E_{c \text{bw}} = 0$ and $\Delta E_{c \text{bw}} = 0.2$ eV (dashed line) and 0.5 eV (solid line).
is presented in Table 3. It can be seen that when S/(S+O) is 0.3, the cell performance is better with $\Delta E_{c}^{ab}$ of 0.2 eV. When sulfur fraction is 0.1, the cell conversion efficiency is inferior to the one with 0.3 sulfur content, which is probably caused by the interfacial recombination with -0.1 eV $\Delta E_{c}^{ab}$. Whereas the cell with sulfur fraction of 0.6 has low FF and $\eta$ for a large $\Delta E_{c}^{ab}$.

### 6. Conclusions

In this study, Zn(O,S) buffer layers have been used in CZTS solar cells. Numerical simulations of CZTS/Zn(O,S) solar cells were investigated by SCAPS. From the simulation results it seems that the composition of Zn(O,S) can modify the CBO at the CZTS/Zn(O,S) interface and affect the cell performance obviously. When $\Delta E_{c}^{ab}$ is in the range of 0.1–0.3 eV with the structure of CZTS/Zn(O,S)/AZO, the cell performance is better. Therefore, Zn(O,S) is a promising material to be used in CZTS-based solar cell as a Cd-free buffer layer.

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### References


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**Table 3. Performance of CZTS/Zn(O,S) cells with different sulfur content**

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{c}^{ab}$</th>
<th>$\Delta E_{c}^{bb}$</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (O$<em>{0.3}$S$</em>{0.1}$)</td>
<td>-0.1</td>
<td>0</td>
<td>0.95</td>
<td>18.47</td>
<td>80.06</td>
<td>14.02</td>
</tr>
<tr>
<td>Zn (O$<em>{0.7}$S$</em>{0.3}$)</td>
<td>0.2</td>
<td>-0.3</td>
<td>0.97</td>
<td>18.65</td>
<td>82.76</td>
<td>14.90</td>
</tr>
<tr>
<td>Zn (O$<em>{0.4}$S$</em>{0.6}$)</td>
<td>0.5</td>
<td>-0.6</td>
<td>0.98</td>
<td>18.03</td>
<td>30.26</td>
<td>5.36</td>
</tr>
</tbody>
</table>


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