Prospects of Zn(O,S) as an alternative buffer layer for Cu_2ZnSnS_4 thin-film solar cells from numerical simulation

Hong Zhang[1,2], *Shuying Cheng*[1,2] ✉, *Jinling Yu*[1,2], *Haifang Zhou*[1,2], *Hongjie Jia*[1,2]

[1]*College of Physics and Information Engineering, and Institute of Micro-Nano Devices and Solar Cells, Fuzhou University, Fuzhou 350108, People's Republic of China*
[2]*Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, Changzhou, 213164, People's Republic of China*
✉ *E-mail: sycheng@fzu.edu.cn*

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Zn(O,S) is an attractive alternative to CdS as a buffer layer of Cu_2ZnSnS_4 (CZTS)-based solar cell due to its higher bandgap and environmental friendliness. In this work, CZTS solar cell with a structure of CZTS/Zn(O,S)/Al:ZnO was simulated by Solar Cell Capacitance Simulator (SCAPS). The impacts of thickness and acceptor concentration of CZTS, thickness and donor concentration of Zn(O,S) and operating temperature on the performance of CZTS solar cells were investigated. It has been obtained that the optimum thickness of CZTS is between 2000 and 3000 nm and that of Zn(O,S) is about 50 nm. The suitable doping concentrations of CZTS and Zn(O,S) layers are around 10^{16} and 10^{17} cm^{-3}, respectively. The temperature coefficient of efficiency is about −0.023 %/K in the CZTS solar cell. All these simulation results will provide some important guidelines for fabricating high efficient CZTS solar cells.

1. Introduction: Cu_2ZnSnS_4 (CZTS) has become a candidate material for new photovoltaic cells recently, because of its suitable bandgap energy of 1.4–1.5 eV and absorption coefficient over 10^4 cm^{-1} [1, 2]. In addition, all the elements of CZTS are naturally abundant and nontoxic. With the development of different techniques employed to fabricate CZTS thin films, the conversion efficiency of CZTS-based solar cells was improved from 0.66% in 1996 [3] to 9.1% in 2014 [4]. In the conventional structure of CZTS solar cell, CdS is used as a buffer layer. However, parasitic absorption in CdS layer is considered to be responsible for the drop of quantum efficiency [5], and a large amount of Cd-containing waste will cause the environmental problem during the deposition process [6]. It is necessary to find an environmental friendly material as a replacement of CdS. Zn (O,S) is a good choice because of its higher bandgap and better collection of short-wavelength photons. High conversion efficiency has been demonstrated for $Cu(In,Ga)Se_2$ (CIGS) thin-film solar cells with Zn(O,S) buffer layer [7]. When Zn(O,S) buffer layers were used in CIGS-based solar cells, better cell performance could be achieved for S/(S + O) atomic ratios of 0.25–0.40 [8–10]. Moreover, CZTS solar cells with Zn(O,S) buffer layers were also obtained with a conversion efficiency of 4.6% [11], when S/(S + O) atomic ratio of Zn(O,S) was 0.3. However, the operation mechanism of Zn(O,S) as a buffer layer in the CZTS solar cell is seldom reported. In this Letter, based on the structure of CZTS/buffer layer/Al:ZnO, the properties of CZTS thin-film solar cells were evaluated by Solar Cell Capacitance Simulator (SCAPS) [12]. The cell performance dependence on a set of physical parameters such as the thickness and acceptor concentration of CZTS, the thickness and donor concentration of buffer layer and operating temperature, was studied.

2. Numerical simulation: Numerical simulation is a useful tool to explore the performance of a solar cell of certain design and thus examine its viability. There are different types of numerical simulators among which SCAPS is capable of properties analysis of hybrid semiconductor structures, such as current voltage characteristics in the dark and under illumination, electric field distributions, free and trapped carrier populations, recombination profiles, individual carrier current densities and so on [13].

Here CZTS thin-film solar cell with the structure of CZTS/buffer layer/Al:ZnO was implemented in the SCAPS 3.3 environment. The S/(S + O) atomic ratio of Zn(O,S) was set to 0.3. The basic input parameters used in the simulation were adopted from literatures, theories, or reasonable estimates in some cases and shown in Table 1. The default illumination spectrum and operation temperature were set to the global AM1.5 standard and 300 K, respectively.

3. Results and discussion
3.1. Impacts of thickness of CZTS absorber layer: By varying the thickness of CZTS absorber layer from 500 to 4000 nm with

Table 1 Parameters used in the simulation

Parameters	CZTS [14–16]	Zn(O,S) [16–18]	CdS [19, 20]	Al:ZnO [21, 22]
thickness, nm	2000	50	50	200
bandgap, eV	1.5	2.7	2.4	3.4
electron affinity, eV	4.5	4.3	4.5	4.6
dielectric permittivity (relative)	6.5	10	10	9
CB effective density of states, $1/cm^3$	2.07×10^{18}	2.2×10^{18}	2×10^{18}	4×10^{18}
VB effective density of states, $1/cm^3$	8.85×10^{18}	1.8×10^{19}	1.5×10^{19}	9×10^{18}
electron mobility, cm^2/Vs	26	100	50	100
hole mobility, cm^2/Vs	10	25	20	31
shallow uniform donor density N_D, $1/cm^3$	–	1×10^{17}	1×10^{17}	1×10^{20}
shallow uniform acceptor density N_A, $1/cm^3$	1×10^{16}	–	–	–

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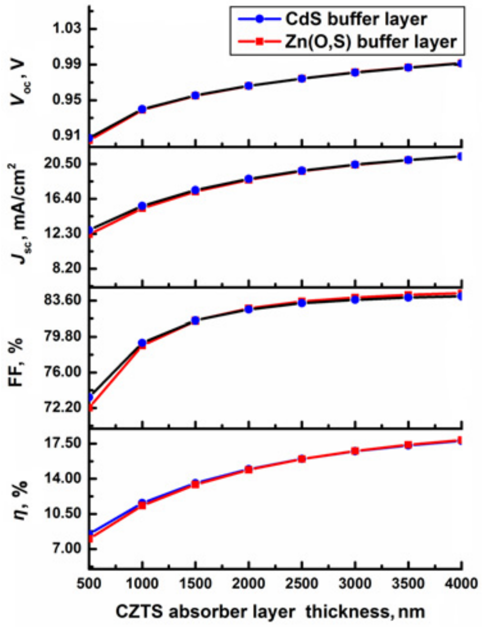

Fig. 1 *Cell performance with various CZTS absorber layer thicknesses*

other input parameters keeping unchanged (shown in Table 1), the cell performance was investigated by SCAPS simulation. Fig. 1 shows the detailed effects of the CZTS layer thickness on the cell performance parameters, such as open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and efficiency (η). It can be seen that all the cell performance parameters increase with increasing CZTS thickness. Figs. 2*a* and *b* show the quantum efficiency of the CZTS solar cell with variable CZTS absorber layer thicknesses. The tendency of parameters for the cell with Zn(O,S) or CdS buffer layer is almost the same. When the CZTS layer is thicker, more photons with longer wavelength can be collected in the CZTS absorber layer. This will contribute to more electron–hole pair generation and collection as the longer wavelength photons can be absorbed. Thus J_{sc} and V_{oc} will increase and finally the efficiency will be improved [18]. However, when the CZTS layer is thicker than 2000 nm, the cell performance cannot be improved significantly. It seems that the electron–hole pairs produced from the absorbed photons at longer wavelength may recombine before reaching the depletion region and being collected. Hence the optimum thickness for CZTS absorber layer is between 2000 and 3000 nm with Zn(O,S) or CdS as a buffer layer, considering the material cost and fabrication process.

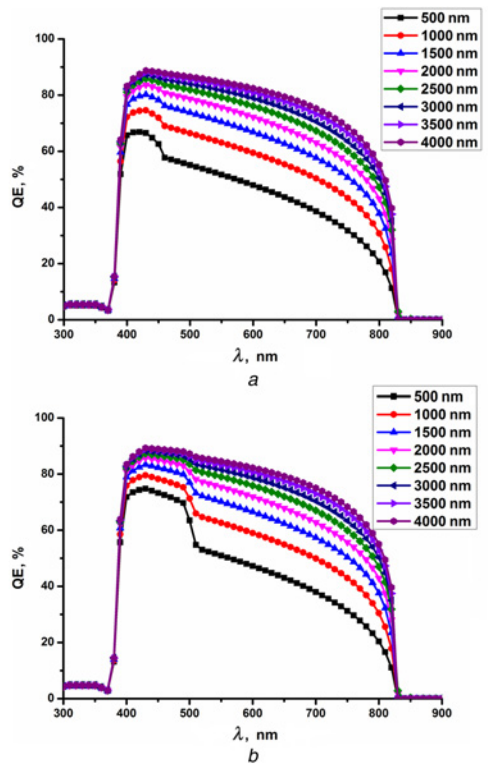

Fig. 2 *Quantum efficiency with different CZTS absorber layer thicknesses with*
a Zn(O,S) buffer layer
b CdS buffer layer

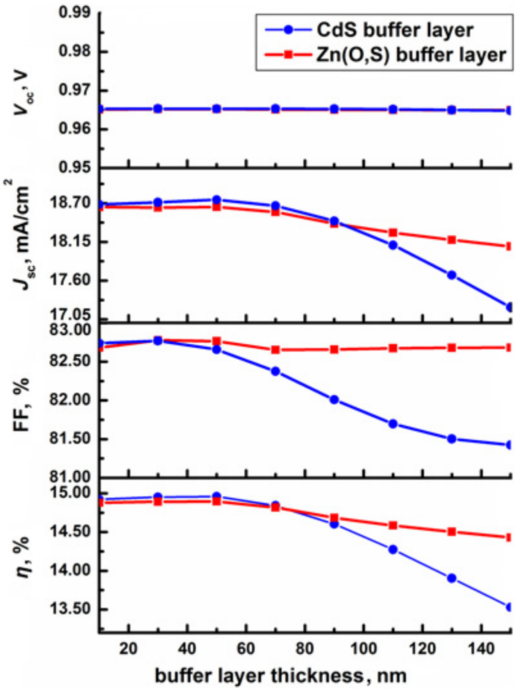

Fig. 3 *Cell performance with various buffer layer thicknesses*

3.2. Impacts of thickness of buffer layer: Setting the thickness of CZTS layer to 2000 nm and keeping other parameters constant (as shown in Table 1), the thickness of buffer layer was varied from 10 to 150 nm. Fig. 3 shows the effect of buffer layer thickness on the cell performance. When the thickness is thinner (<50 nm), the cell performance changes little. When the thickness of buffer layer increases (>50 nm), V_{oc} is almost constant, but J_{sc} and η decrease. It seems that more photons are absorbed by the buffer layer and there are fewer photons reaching the CZTS absorber layer and contributing to the quantum efficiency (as shown in Figs. 4*a* and *b*), when the buffer layer is thicker. This may lead to the drop of J_{sc}. Too thin buffer layer may cause the leakage current of CZTS solar cells. It suggests that the optimal thickness of Zn(O,S) or CdS buffer layer is about 50 nm, considering the cell efficiency and the lattice mismatch between the buffer layer and CZTS.

3.3. Impacts of acceptor concentration of CZTS absorber layer: The thicknesses of absorber and buffer layers are set to 2000 and 50 nm, respectively. Fig. 5 shows the effect of acceptor concentration of CZTS layer on the cell performance. V_{oc} increases, but J_{sc} decreases with increasing acceptor concentration. It could be explained that increasing the carrier concentration of CZTS layer

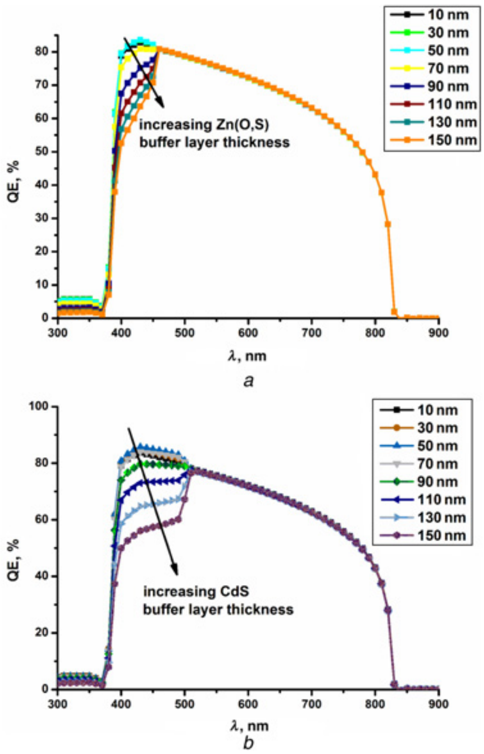

Fig. 4 *Quantum efficiency with different*
a Zn(O,S) buffer layer thicknesses
b CdS buffer layer thicknesses

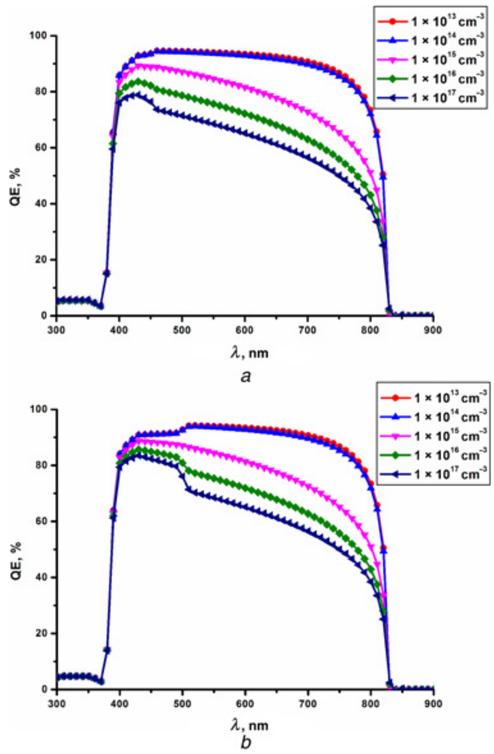

Fig. 6 *Cell quantum efficiency with different CZTS carrier concentrations*
a With Zn(O,S) buffer layer
b With CdS buffer layer

could decrease the space charge region width. Thus the electric field in the depletion layer increases, resulting in the increment of V_{oc}. However, if the acceptor concentration is higher, the carrier recombination in the bulk increases. This may result in low quantum efficiency of long wavelength photons (as shown in Figs. 6*a* and *b*), which are absorbed deeper in CZTS so that the generated carriers are more dependent on the diffusion effect to be collected effectively [14]. Thus J_{sc} drops [22]. When the absorber doping concentration is about 10^{16} cm^{-3}, the conversion efficiency is better. Therefore the acceptor concentration of CZTS layer shall be around 10^{16} cm^{-3}.

3.4. Impacts of donor concentration of buffer layer: The doping of buffer layer is an important parameter. In Fig. 7 V_{oc}, J_{sc}, FF and η curves are plotted against the donor concentration of buffer layer, with 2000-nm-thick absorber layer, 50-nm-thick buffer layer and other input parameters unchanged. When the donor concentration is low (<10^{15} cm^{-3}), the change of V_{oc}, J_{sc}, FF or η is

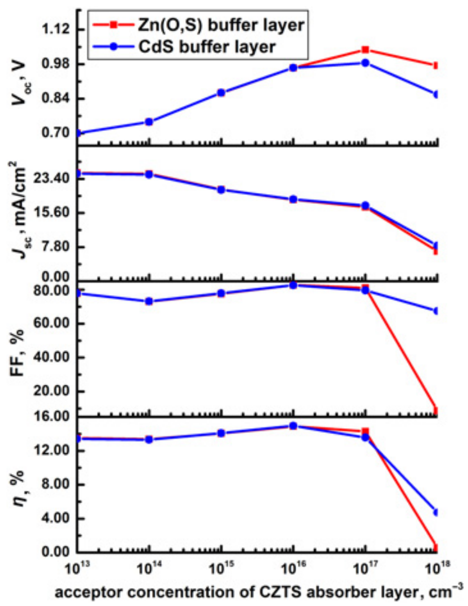

Fig. 5 *Cell performance with various CZTS absorber doping concentrations*

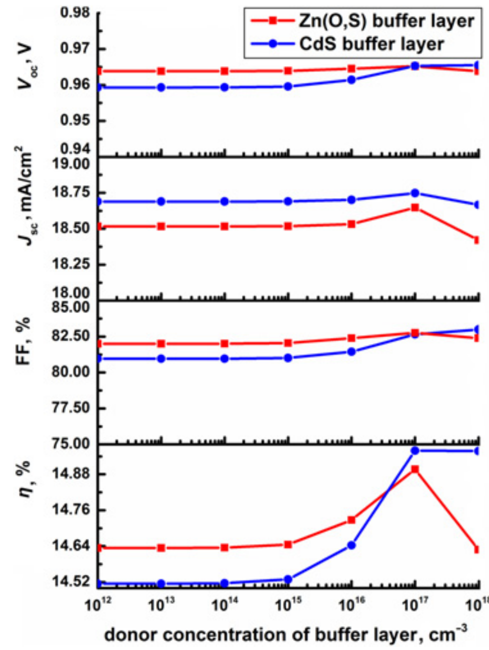

Fig. 7 *Cell performance with various buffer layer donor concentrations*

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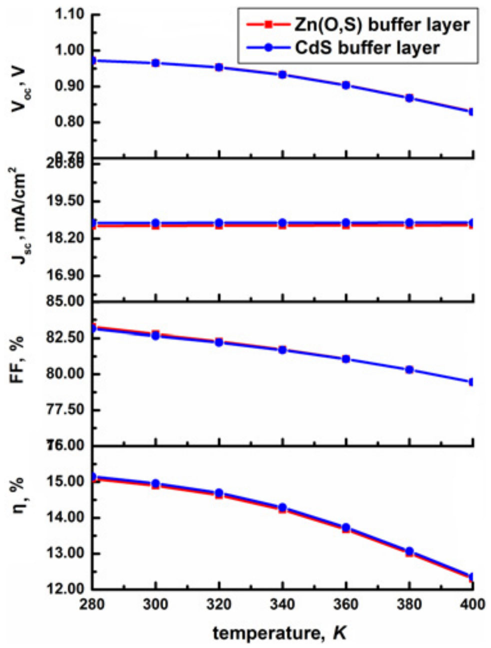

Fig. 8 *Cell performance with different operation temperatures*

insignificant. However, J_{sc} and η are clearly improved for higher donor concentration. This suggests that the increase in doping concentration of buffer layer would increase the electric field in the hetero-junction, thus increasing the collection of photo-generated electron–hole pairs. However, when the donor concentration of buffer layer is above $10^{17}\,cm^{-3}$, J_{sc} have a downward trend. It seems that the carrier recombination in the bulk increases when the donor concentration is higher. Thus the suitable donor concentration of Zn(O,S) or CdS layer is about $10^{17}\,cm^{-3}$.

3.5. Impacts of operating temperature: Operating temperature plays a vital role in the performance of solar cells as the solar cells can be heated up under the sun. Fig. 8 shows the influences of the temperature on the properties of CZTS solar cells. V_{oc}, FF and η decrease and J_{sc} changes little with the temperature increasing from 280 to 400 K. As the temperature is higher, the reverse saturation current rises which may result in the drop of V_{oc}. When the operating temperature rises, electrons in the solar cell gain additional energies and are more likely to recombine with holes before they reach the depletion region. Then more electron–hole pairs generate under high operating temperature. Thereby the variation of J_{sc} is relatively small. The reduction in V_{oc} leads to drop of the efficiency as the temperature increases. Moreover, the temperature coefficient of the conversion efficiency for CZTS solar cells with Zn(O,S) or CdS buffer layer is found to be about −0.023%/K. It can be seen that the CZTS solar cells with Zn(O, S) buffer layers are stable at a lower operating temperature.

3.6. Optimisation of the CZTS solar cell: The thicknesses of CZTS absorber and buffer layers are set to 2000 and 50 nm, respectively. The acceptor concentration of CZTS layer and the donor concentration of buffer layer are set to 1×10^{16} and $1 \times 10^{17}\,cm^{-3}$ respectively. The temperature of the solar cell is set to 300 K. Other parameters are kept unchanged as shown in Table 1. From the simulation, the optical conversion efficiencies for Zn(O,S) and CdS buffer layers are about 14.90 and 14.97%, respectively, which are shown in Fig. 9. It indicates that Zn(O,S) is a potential alternative to CdS as a buffer layer of CZTS-based solar cell.

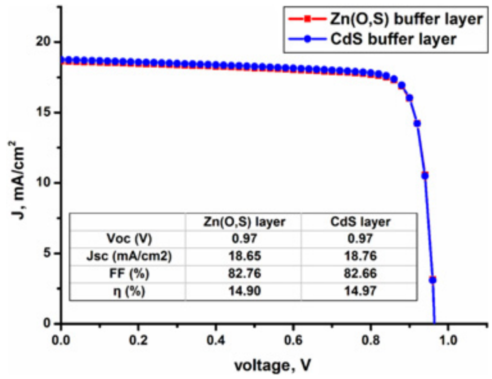

Fig. 9 *Simulated J–V characteristics of optimised CZTS cell with Zn(O,S) and CdS buffer layers*

4. Conclusion: As one of candidate materials for Cd-free buffer layers, Zn(O,S) can be used in the CZTS solar cell. In this Letter, a comprehensive numerical simulation of CZTS solar cell with Zn(O,S) buffer layer, whose S/(S + O) atomic ratio was 0.3, was investigated by SCAPS computer software. The influence of CZTS absorber layer thickness, acceptor concentration, buffer layer thickness, donor concentration and operating temperature on the solar cell performance was investigated. An optimum CZTS thickness is around 2000–3000 nm. The suitable thickness of Zn (O,S) buffer layers is about 50 nm. The appropriate doping concentrations of CZTS and Zn(O,S) are about 10^{16} and $10^{17}\,cm^{-3}$ respectively. The temperature coefficient of the conversion efficiency is about −0.023%/K and the CZTS solar cell is relatively stable. The simulation results show that the efficiency of CZTS/Zn(O,S) solar cells can be 14.90%, which is similar to the cell with CdS buffer layer. It can be seen that Zn (O,S) is a very promising Cd-free buffer layer to be used in CZTS-based solar cell.

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