Numerical modeling of ZnSnO/CZTS based solar cells

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Numerical simulation has been performed to improve the performance of Cu_2ZnSnS_4 (CZTS) solar cells by replacing CdS with $Zn_{1-x}Sn_xO$ buffer layer. The influences of thickness, donor concentration and defect density of buffer layers on the performance of CZTS solar cells were investigated. It has been found that $Zn_{1-x}Sn_xO$ buffer layer for Sn content of 0.20 is better for CZTS solar cell. A higher efficiency can be achieved with thinner buffer layer. The optimized solar cell demonstrated a maximum power conversion efficiency of 13%.

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A promising absorber material for thin film solar cells, known as kesterite, Cu_2ZnSnS_4 (CZTS), was used for its low toxicity, natural abundance, excellent light absorption and higher theoretical efficiency[1]. Only 11% efficiency of CZTS thin-film solar cells has been achieved by 2018[2]. However, this efficiency is quite less in comparison to that of $CuIn_xGa_{1-x}Se_2$ (CIGS) (22.6%)[3] and CdTe (22.1%)[4]. In the case of CZTS-based solar cells, non-radiative bulk (CZTS absorber layer) and interface recombination (CdS/CZTS and CZTS/Mo) are the major electrical losses, which are accordingly considered as performance limiters[1].

The conduction band offset (*CBO*) at CdS/CZTS interface plays an essential role in the performance of kesterite solar cells. Various studies have focused on reducing heterojunction recombination at this interface using experimental, theoretical and computational approaches. COUREL et al[5] have demonstrated theoretically and experimentally that interface recombination has a major impact on CdS/CZTS heterojunction due to "cliff-like" alignment and the tunneling enhanced recombination via this interface was found to be the main transport mechanism leading to low open-circuit voltage (V_{OC}) values[6]. For improving the value of V_{OC}, YAN et al[2] have used heat treatment at CdS/CZTS interface, which improved the V_{OC} by about 730 mV , and reducing the *CBO* at −0.04 eV is cliff type. LIU et al[7] have doped CZTS layer with Na (CZTS:Na), which remarked that after doping-Na on the CZTS surface, the cliff-like *CBO* is reduced from 0.25 eV to 0.1 eV and the cell performance is enhanced. There are other ways to reduce the recombination at CdS/CZTS interface and enhance the cell performance of kesterite solar cell. The researchers replaced the CdS layer with an environmentally friendly buffer layer in order to obtain a non-toxic solar cell[1]. CROVETTO et al[8] have demonstrated that Zn-based alternative buffer layers are advantageous on cell performance of CZTS solar cell, owing to the capacity of Zn to passivate surface states. The high efficiency reported is 9.3% using ZnSnO (ZTO) buffer layer on CZTS solar cell[9]. In this work, we propose to compare the effects of CdS and ZTO buffer layers on the cell performance of CZTS thin film solar cells.

In previous works, the importance of numerical modeling to improve the performance of thin-film solar cells has been demonstrated[1,10,11]. One of the important programs simulating solar cells is SCAPS-1D[12].

Our conventional structure used was based on recent work with bulk CZTS defects, with material parameters taken from Ref.[11] (see Tab.1). Fig.1 compares experimental data[13] and our conventional device based on the material properties outlined in Ref.[11]. The simulation and experimental performance parameters including V_{OC}, short-circuit current density (J_{SC}), fill-factor (*FF*) and efficiency (η) are summarized in Fig.1(a). Quantum efficiency as a function of wavelength for CZTS solar cells is shown in Fig.1(b). Comparison of simulation findings with experimental data demonstrates an acceptable basis for our study which validates our modeling.

A number of Cd-buffer layers of CZTS solar cell have been study numerically like ZnS, ZnMgO and ZnOS[14,15]. However, no work has studied the effect of ZTO buffer layer on the performance of CZTS solar cell. Fig.2(a) shows a schematic of the band variations for the $Zn_{1-x}Sn_xO$ semiconductor[16]. Fig.2(b) shows the absorption coefficient of the $Zn_{1-x}Sn_xO$ determined experimentally[9]. The absorption coefficient was calculated from the well-known relation $\alpha=4\pi k/\lambda$, where k represents the imaginary part of the complex dielectric constant and λ is the light wavelength.

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Tab.1 Material parameters used in the simulation[11]

Material properties	Unit	ZnO: Al	ZnO	CdS	CZTS	MoS_2
Thickness (μm)	μm	0.45	0.08	0.08	0.6	0.11
Relative dielectric permittivity ε	-	9	9	9	7	10
Bandgap E_g	eV	3.4	3.27	2.40	1.45	1.3
Electron affinity χ	eV	4.51	4.5	4.11	4.32	4.5
CB effective density of states N_C	cm^{-3}	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}	2.2×10^{18}
VB effective density of states N_V	cm^{-3}	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}	1.8×10^{19}
Electron mobility μ_e	$cm^2/V\cdot s$	100	100	100	6	100
Hole mobility μ_h	$cm^2/V\cdot s$	25	25	20	10	25
Donor (Acceptor) density $N_{D(A)}$	cm^{-3}	1×10^{21}	1×10^{18}	1×10^{18}	1×10^{16}	2.5×10^{18}
Defect density N_t	cm^{-3}	10^{15}	10^{15}	10^{18}	10^{13}	-

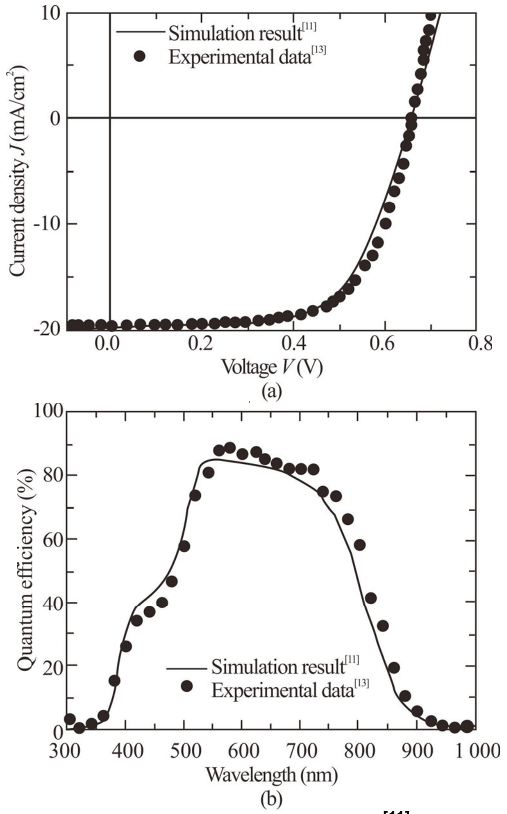


Fig.1 Comparison between simulated[11] and experimental[13] characteristics of CZTS solar cell: (a) *J-V* characteristics; (b) Quantum efficiency

The replacement of the CdS by a $Zn_{1-x}Sn_xO$ buffer layer caused modifications in the basic model. However, the *CBO* of $Zn_{1-x}Sn_xO$/CZTS heterojunction varied (see Fig.3). There are two different heterojunctions formed at the buffer/CZTS interface with a positive *CBO* (called "spike") and a negative *CBO* (called "cliff").

The effect of composition ratio Sn/(Zn+Sn) of $Zn_{1-x}Sn_xO$ buffer layer on the performance of CZTS solar cells in relation to the conventional cell with the CdS buffer layer is presented in Fig.4. A strong dependence of the cell performance on the buffer composition is observed. The V_{OC} increased with the increasing incorporation of Sn. As shown, when the *CBO* increased from cliff to spike, the V_{OC} increased. When cliff formed, a high cross-interface recombination improved. In general, $Zn_{1-x}Sn_xO$/CZTS devices can achieve a higher J_{SC} than the CdS/CZTS based device, as illustrated in Fig.4. This is mainly due to higher absorption in the short wavelength range, as shown in Zone 1 of the quantum efficiency curves presented in Fig.5, as well as can be attributed to a higher transparency of the $Zn_{0.80}Sn_{0.20}O$ film (e.g. 3 eV) compared to the reference buffer layer CdS (e.g. 2.4 eV). In addition, there is also absorption loss for $Zn_{0.80}Sn_{0.20}O$/CZTS in the wavelength of Zone 2, which may be depending on the quality of the interface buffer/CZTS. Consequently, it was found that the conversion efficiency of all CZTS/ZTO cells with an Sn content from 0.18 to 0.31 is higher than that of the CdS based device, due to the contribution of a higher J_{sc}. The $Zn_{0.80}Sn_{0.20}O$ buffer layer has achieved the high efficiency of ~9%.

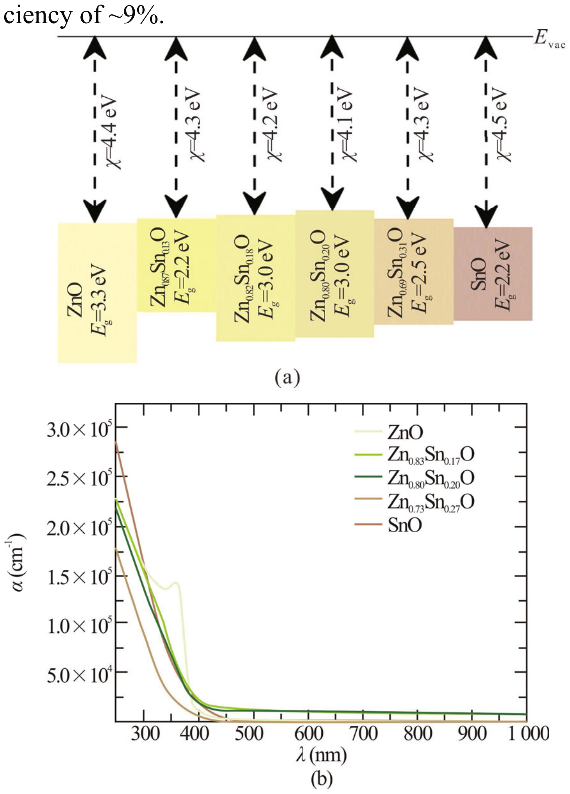


Fig.2 (a) Schematic of the band variations for the $Zn_{1-x}Sn_xO$[16]; (b) Absorption coefficient of the $Zn_{1-x}Sn_xO$[9]

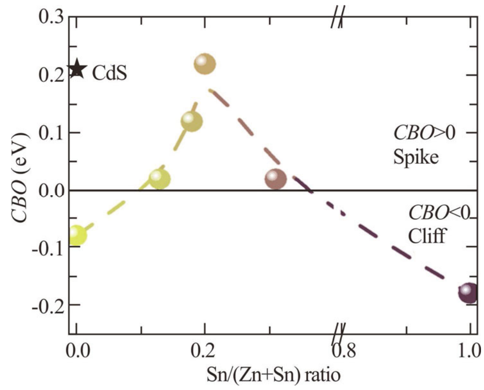


Fig.3 ***CBO*** **of CdS/CZTS and $Zn_{1-x}Sn_xO$/CZTS hetero-junction**

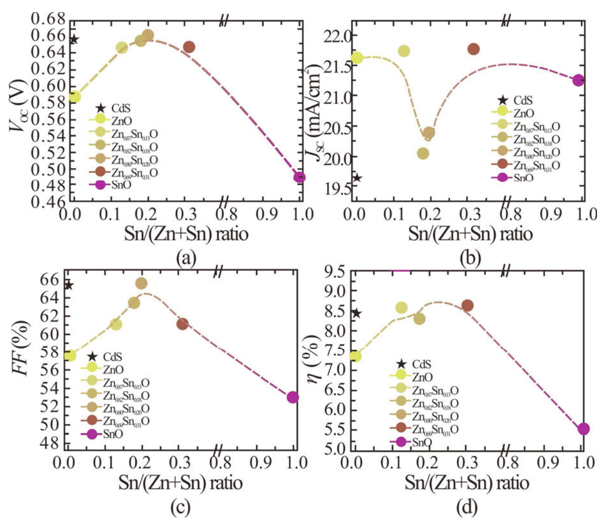


Fig.4 Effect of composition ratio Sn/(Zn+Sn) of $Zn_{1-x}Sn_xO$ buffer layer on the performance of CZTS solar cells: (a) V_{OC}; (b) J_{SC}; (c) *FF*; (d) η

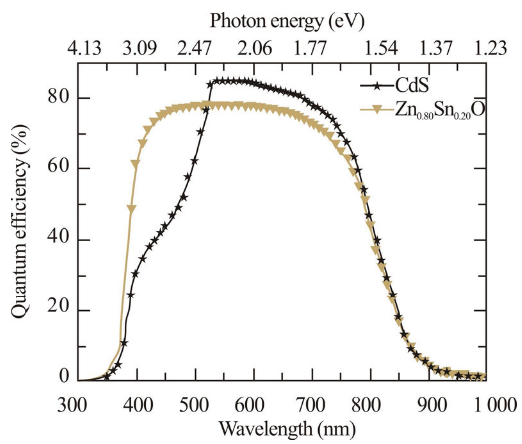


Fig.5 Quantum efficiency curves for CdS and $Zn_{0.80}Sn_{0.20}O$

For the following studies, we will optimize the properties of the $Zn_{1-x}Sn_xO$ buffer layer for Sn content of 0.20.

The simulated results of cell performance and quantum efficiency curves for varying thicknesses from 0.02 μm to 0.1 μm of CdS and $Zn_{0.80}Sn_{0.20}O$ are shown in Fig.6 and Fig.7, respectively. As the thickness of the buffer layer increases, J_{SC} decreases. This means that more photons are absorbed by the buffer layer and there are fewer photons reaching the CZTS absorber layer. It can see that an increase in the thickness of the buffer layer causes a drop in the blue response of the quantum efficiency due to the increased absorption in the CdS layer. It is remarked that $Zn_{0.80}Sn_{0.20}O$ buffer layer based device has better performance compared with CdS based device. However, the high efficiency achieved is 9.4% at thickness of 0.02 μm for $Zn_{0.80}Sn_{0.20}O$ layer. So, the thinner $Zn_{0.80}Sn_{0.20}O$ buffer contributes the better blue response than CdS buffer.

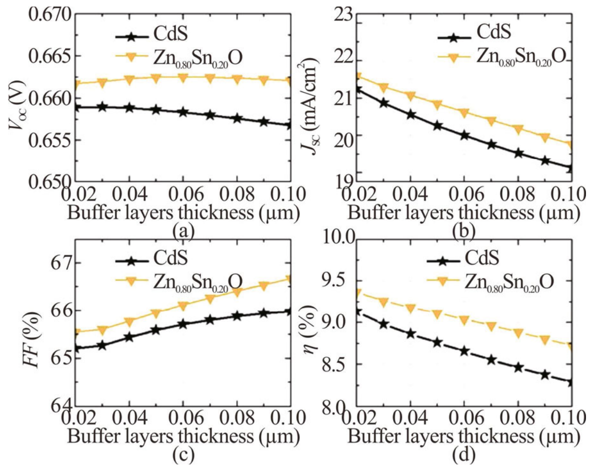


Fig.6 Effects of buffer layer thicknesses on the performance of CZTS solar cells: (a) V_{OC}; (b) J_{SC}; (c) *FF*; (d) η

The carrier concentration of ZTO increases with the Sn concentration, reaches a maximum value and then decreases[17]. The simulated results of cell performance and quantum efficiency curves for varying donor concentration from 10^{16} cm^{-3} to 10^{19} cm^{-3} of CdS and $Zn_{0.80}Sn_{0.20}O$ are shown in Fig.9 and Fig.10, respectively. When increasing the donor concentration of the buffer layers, the barrier at the absorber/buffer interface is reduced (Fig.11). As result, V_{oc}, *FF*, and η increased. Contrarily, by increasing the carrier concentration, the diffusion length of the charge carriers' decreases and this leads to a decrease in the value of J_{SC}[18].

The simulated results of cell performance and quantum efficiency curves for varying defect density from 10^{15} cm^{-3} to 10^{18} cm^{-3} of CdS and $Zn_{0.80}Sn_{0.20}O$ are shown in Fig.12 and Fig.13, respectively. An increase of the total trap density of the acceptor-like mid-gap defects in the bulk region of the buffer layer will cause an enhancement of the recombination current (Fig.14). The rise of the defects density brings to a deterioration of the solar cell performance. From these results, the quality of deposition of ZTO is very important.

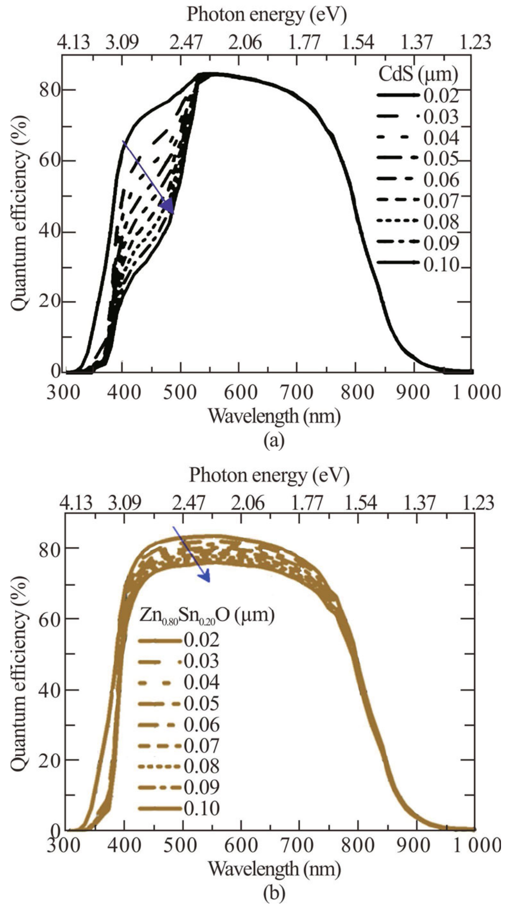


Fig.7 Effects of thicknesses of (a) CdS and (b) $Zn_{0.80}Sn_{0.20}O$ buffer layers on quantum efficiency

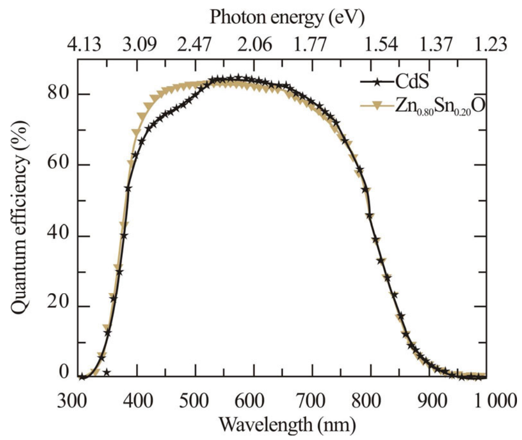
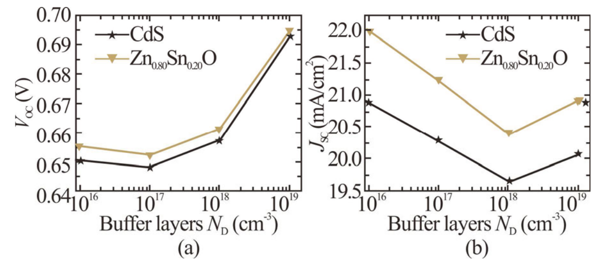


Fig.8 Quantum efficiency curve comparison for CdS and $Zn_{0.80}Sn_{0.20}O$ buffer layers with the same thickness of 0.02 μm



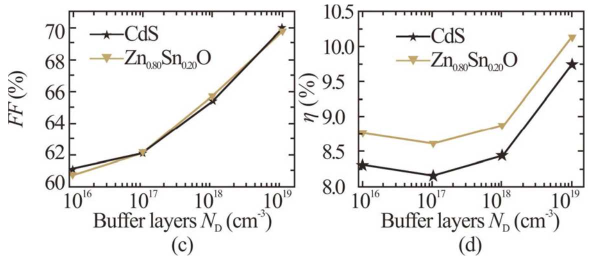


Fig.9 Effects of donor concentrations of CdS and $Zn_{0.80}Sn_{0.20}O$ buffer layers on the performance of CZTS solar cells: (a) V_{OC}; (b) J_{SC}; (c) *FF*; (d) *η*

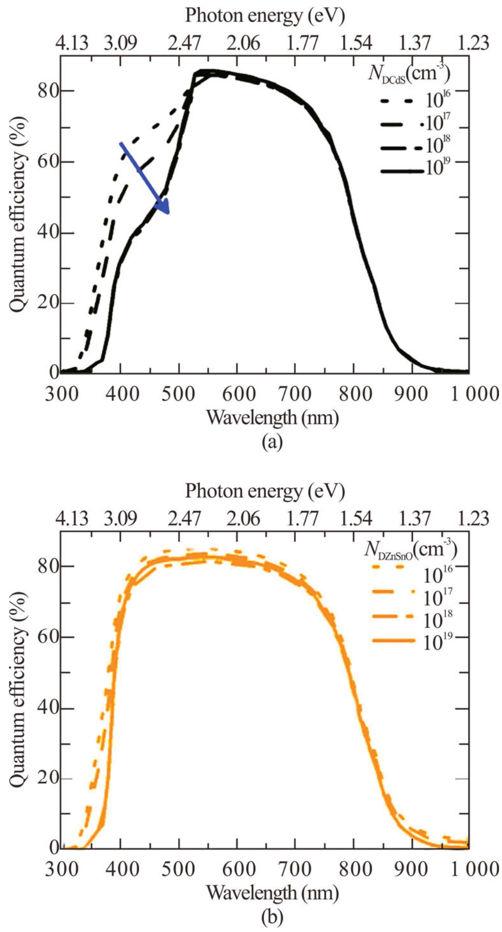
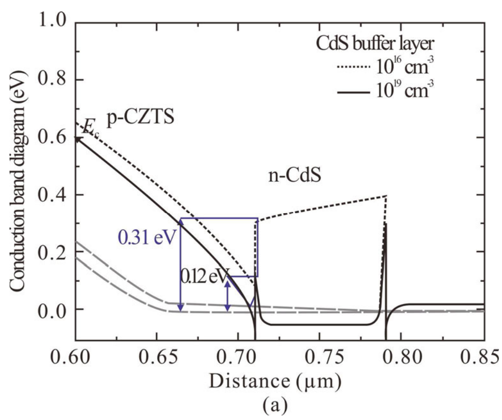


Fig.10 Effects of donor concentrations of (a) CdS and (b) $Zn_{0.80}Sn_{0.20}O$ buffer layers on quantum efficiency



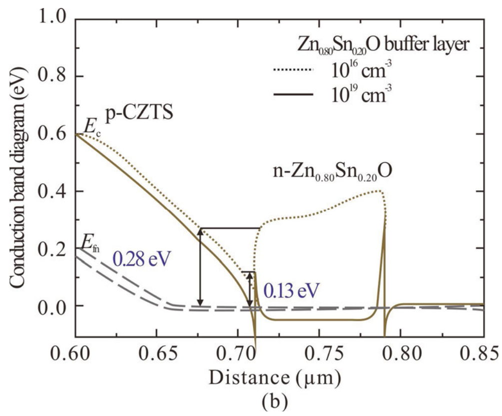


Fig.11 Effects of donor concentrations of (a) CdS and (b) $Zn_{0.80}Sn_{0.20}O$ buffer layers on conduction band diagram

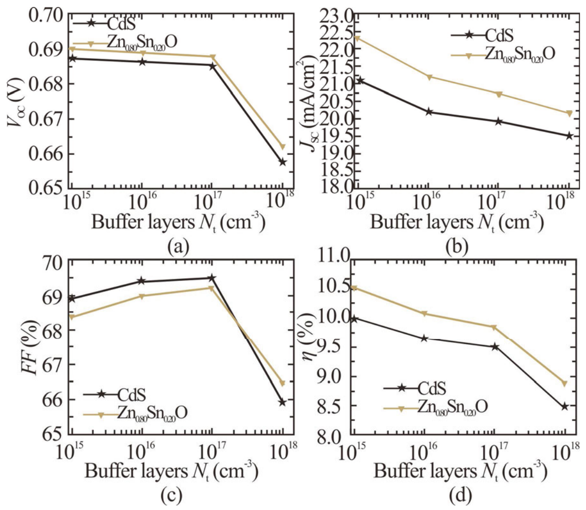


Fig.12 Effects of defect densities of CdS and $Zn_{0.80}Sn_{0.20}O$ buffer layers on the performance of CZTS solar cells: (a) V_{OC}; (b) J_{SC}; (c) FF; (d) η

From the above study, buffer layer thickness of 0.02 μm, donor concentration of 10^{18} cm^{-3} and defect density of 2×10^{16} cm^{-3} have been considered as optimized parameters for the best cell performance of the CZTS device. Other parameters are kept unchanged. In addition, we have eliminated buffer/CZTS interface and series resistance R_S. From the simulation, the high efficiency achieved is 13.23% for $Zn_{0.80}Sn_{0.20}O$. The simulated and experimentally reported results are shown in Tab.2.

Experimentally, the high efficiency has been achieved with a thinner ZTO layer and "spike-like" *CBO*[9,21,22]. The thicker ZTO buffer layer with high resistivity could contribute directly to the overall R_s and result in loss of *FF*[9]. For reducing interface recombination between ZTO and CZTS, a thin layer was deposited like Zn(O,S), Al_2O_3 and CdS [9,23,24].

In conclusion, this study compared the influence of the replacement of CdS by the $Zn_{1-x}Sn_xO$ buffer layer on the performance of CZTS solar cells using the one-dimensional simulator SCAPS-1D. The effect of composition ratio Sn/(Zn+Sn) of $Zn_{1-x}Sn_xO$ buffer layer on the performance of CZTS solar cells was presented. The effects of the thickness, donor concentration and defect density for the buffer layer have also been investigated to improve cell performance and quantum efficiency. A $Zn_{0.80}Sn_{0.20}O$ buffer layer with a thickness of 0.02 μm has been confirmed to be suitable to give the best performance of the device. From this, we can see that $Zn_{0.80}Sn_{0.20}O$ is a very promising Cd-free buffer layer for CZTS-based solar cells.

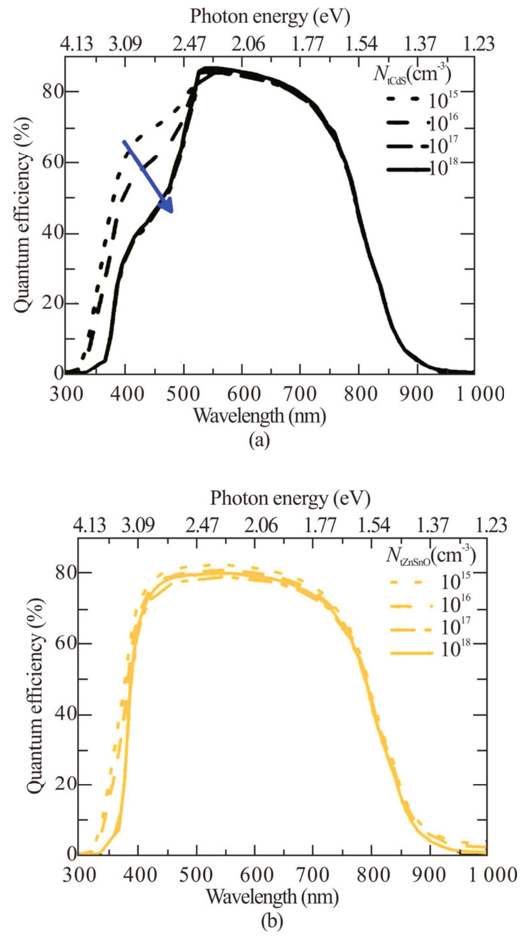


Fig.13 Effects of defect densities of (a) CdS and (b) $Zn_{0.80}Sn_{0.20}O$ buffer layers on quantum efficiency

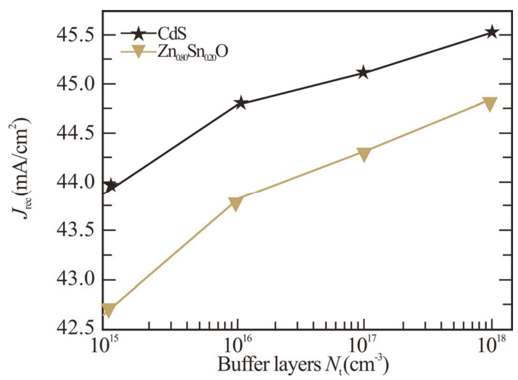


Fig.14 Effects of defect densities of (a) CdS and (b) $Zn_{0.80}Sn_{0.20}O$ buffer layers on recombination current J_{rec}

Tab.2 Optimized and experimental output performance of buffer/CZTS solar cells

	Structure	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF* (%)	η (%)
This work	ZnO:Al/i-ZnO/CdS (0.02 μm)/CZTS/Mo	0.67	21.94	67.71	10.07
	Without interface buffer/CZTS	0.70	22.81	68.81	10.94
	Without R_s and interface	0.70	22.88	81.19	12.94
	ZnO:Al/i-ZnO/ZTO (0.02 μm)/CZTS/Mo	0.67	22.32	67.53	10.23
	Without interface buffer/CZTS	0.70	23.29	68.60	11.15
	Without R_s and interface	0.70	23.36	81.25	13.23
Experimental data	ZnO:Al/ZTO (0.05 μm)/CZTS/Mo[19]	0.721	14.0	51.4	5.2
	ZnO:Al/i-ZnO/ZTO (0.04 μm)/CZTS/Mo[20]	0.682	17.9	60.2	7.4
	ZnO:Al/i-ZnO/ZTO (0.01 μm)/CZTS/Mo[21]	0.679	21.6	61.4	9.0
	ITO/i-ZnO/ZTO (0.01 μm)/CZTS/Mo[9]	0.720	20.5	63.5	9.3
	ZnO:Al/i-ZnO/ZTO (0.028 μm)/CZTS/Mo[22]	0.746	19.1	68.0	9.7
	ZnO:Al/i-ZnO/ZTO/CdS (0.01μm)/CZTS/Mo[23]	0.790	17.3	58.0	7.9
	ZnO:Al/i-ZnO/ZTO/Al_2O_3/CZTS/Mo[24]	0.736	21.0	65.8	10.2

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Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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