

Numerical analysis of $\text{Cu}_2\text{ZnSnS}_4$ thin film solar cells using novel buffer layers

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In order to develop completely nontoxic $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) solar cells, a-Si and $\mu\text{-3C-SiC}$, which possess passivation property, were considered as alternative buffer layer materials to replace the currently used toxic CdS. The effects of the buffer layer choices on the cell performance were investigated by numerical simulations. The quantum efficiency was calculated to understand its dependence on buffer thicknesses. It is found that the thickness of a-Si buffer has significant impact on cell property. The a-Si buffer layer should not be too thick for higher conversion efficiency. Using $\mu\text{-3C-SiC}$ as the buffer layer can significantly improve the blue light response of the CZTS solar cell. Our contribution may open up a new route to Cd-free cells by using amorphous or microcrystalline semiconductors to replace the toxic CdS buffer layer.

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1. Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films are an attractive solar cell absorber material due to its excellent material properties such as a suitable bandgap of about 1.5 eV and large optical absorption coefficient ($\alpha > 10^4 \text{ cm}^{-1}$) [1-4]. Moreover, CZTS is considered to be an environmentally friendly semiconductor since its constituent elements are nontoxic and in great abundance on earth [5,6]. Thus, CZTS is a very promising absorber material for low-cost and sustainable thin film solar cells. However, the typical CZTS thin film solar cells are equipped with a thin CdS buffer layer. It is well known that the cadmium element is toxic so that it can harm to humans and the environment. Therefore, in order to fabricate a completely nontoxic solar cell, alternative buffer materials should be used to replace the toxic CdS buffer layer.

Up to now, some Cd-free materials, such as ZnS [7], ZnSe [8,9], In_2S_3 [10,11], etc [12,13], have been used as the buffer layers for these chalcopyrite solar cells. But, these alternative buffer materials can bring about high interface states which would deteriorate the cell performance. So, Shen et al. [14] introduced the nontoxic amorphous silicon (a-Si) film as the buffer of CZTS solar cells. Employing a-Si as buffer layer can improve the bandgap mismatch of CZTS and window layer, and passivate the surface of CZTS film [14]. While a-Si buffer may result in optical loss in short-wavelength region because of its relatively narrow bandgap (about 1.8 eV), large optical absorption coefficient and very low mobility. For these disadvantages, the microcrystalline cubic silicon carbide ($\mu\text{-3C-SiC}$) thin film may be a

more suitable buffer material since it has low absorption coefficient and relatively wide bandgap (2.2 eV) while retaining the passivation property [15].

In order to understand the performance of CZTS thin film solar cells with two novel buffer layers, a simulation study on CZTS solar cells with a-Si and $\mu\text{-3C-SiC}$ buffers was carried out. The influence of different buffer layers on the cell performance was compared. The cause of changing the cell performance for different buffer layers was analyzed.

2. Methodologies

Fig. 1 shows the schematic structure of the CZTS cell in this work. The cell contains a glass substrate, Mo back contact, p-type CZTS absorber, n-type buffer, n-type ZnO window, Anti-Reflection Coating (ARC) and grid contact. The SCAPS simulator [16-18] is used in this study. The simulation method of the SCAPS program is based on the Poisson equation, the electron and hole continuity equations, and the electron and hole current density equations shown as below respectively [19-20]:

$$\frac{\partial}{\partial x} \left(\varepsilon \frac{\partial \Psi}{\partial x} \right) = -\rho \quad (1)$$

where Ψ is the electrostatic potential, ε is the dielectric permittivity of semiconductor, ρ is the space charge density.

$$\frac{1}{q} \left(\frac{\partial J_n}{\partial x} \right) = -G + R \quad (2)$$

$$\frac{1}{q} \left(\frac{\partial J_p}{\partial x} \right) = G - R \quad (3)$$

where J_n and J_p are the electron and hole current density, respectively, G is the generation rate, and R is the recombination rate.

$$J_n = qn\mu_n \left(\frac{\partial E_{Fn}}{\partial x} \right) \quad (4)$$

$$J_p = qp\mu_p \left(\frac{\partial E_{Fp}}{\partial x} \right) \quad (5)$$

where n and p are the concentrations of free electrons and holes, μ_n and μ_p are the electron and hole mobilities, E_{Fn} and E_{Fp} are the quasi-Fermi levels for electrons and holes, and q is the electron charge.

Then, the solutions to Eqs. (1), (2) and (3) should satisfy the following boundary conditions:

$$J_n = -qS_n (n - n_{eq}) \quad (6)$$

$$J_p = -qS_p (p - p_{eq}) \quad (7)$$

where S_n and S_p are the surface recombination velocities of holes and electrons, and n_{eq} and p_{eq} are the equilibrium concentrations of holes and electrons at the boundaries, respectively.

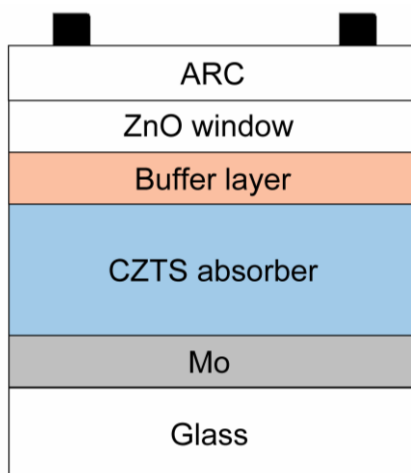


Fig. 1. Schematic structure of the CZTS solar cell in this study.

The basic parameters used in the simulation are shown in Table 1 [21-24]. The simulated illumination is AM 1.5G, 100 mW/cm². The default operation temperature is set to 300 K. The optical absorption coefficients of CZTS and μ c-3C-SiC are taken from Ref. [14,25] and [22], respectively, and those of other materials are obtained from SCAPS program file. In order to study the effect of surface passivation of buffer layers on the cell performance, the interface between the CZTS layer and the buffer layer is added. The interface states vary from 5×10^9 cm⁻² to 10^{11} cm⁻². Fig. 2 illustrates the calculated equilibrium energy band diagram of the CZTS solar cell when the buffer layers are CdS, a-Si and μ c-3C-SiC.

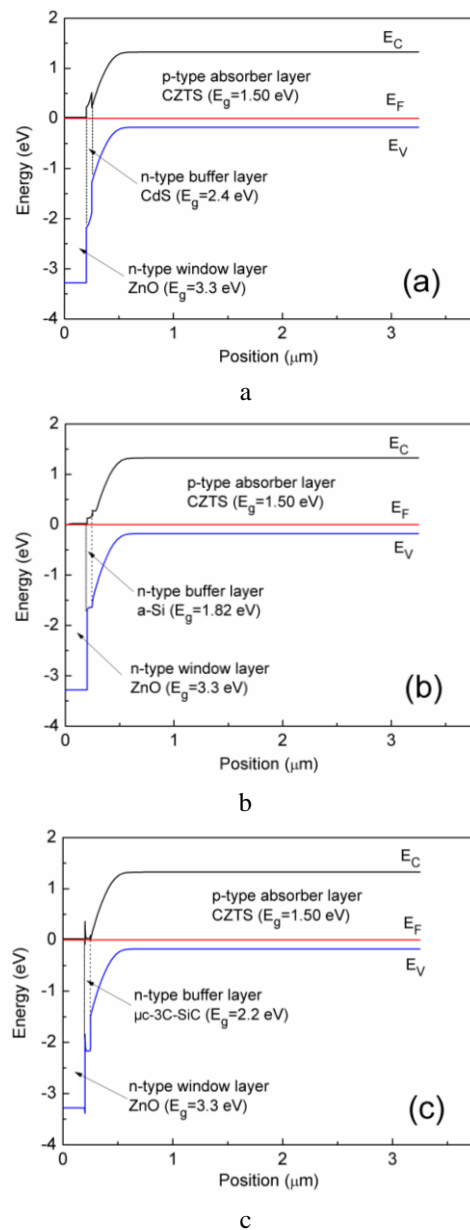


Fig. 2. Equilibrium energy band diagram of the CZTS solar cell when the buffer layers are CdS, a-Si and μ c-3C-SiC.

Table 1. Basic parameters for the simulation of CZTS solar cells.

Parameters and units	ZnO	μc-3C-SiC	a-Si	CdS	CZTS
Thickness (nm)	200	Varied	Varied	Varied	3000
Relative dielectric constant	9	9.72	11.9	10	13.6
Electron mobility (cm ² V ⁻¹ s ⁻¹)	100	20	20	100	100
Hole mobility (cm ² V ⁻¹ s ⁻¹)	25	2	2	25	25
Donor concentration (cm ⁻³)	1×10 ¹⁸	1×10 ¹⁸	3×10 ¹⁸	1×10 ¹⁷	—
Acceptor concentration (cm ⁻³)	—	—	—	—	2×10 ¹⁶
Band gap (eV)	3.3	2.2	1.82	2.4	1.5
Effective conduction band density (cm ⁻³)	2.2×10 ¹⁸	1.5×10 ¹⁹	2.5×10 ²⁰	2.2×10 ¹⁸	2.2×10 ¹⁸
Effective valence band density (cm ⁻³)	1.8×10 ¹⁹	1.2×10 ¹⁹	2.5×10 ²⁰	1.8×10 ¹⁹	1.8×10 ¹⁹
Electron affinity (eV)	4.45	4.0	3.8	3.8	4.1
Peak density of Gaussian defects (cm ⁻³)	10 ¹⁷	10 ¹⁸ , 10 ¹⁸ (double Gau.)	8×10 ¹⁸ , 8×10 ¹⁸ (double Gau.)	10 ¹⁸	10 ¹⁴
Peak energy for Gaussian defects (eV)	1.65	0.7, 0.14	0.6, 1.2	1.2	0.75
Standard deviation for Gaussian defects (eV)	0.1	0.25, 0.25	0.15, 0.15	0.1	0.1

3. Results and discussion

Fig. 3a shows the short-circuit current density J_{sc} as a function of the buffer thickness with different buffer materials. It is shown that J_{sc} decreases obviously from 25.48 mA/cm² to 17.65 mA/cm² when the buffer thicknesses vary from 10 nm to 100 nm if a-Si acts as buffer role. For the cell with CdS buffer, J_{sc} is reduced from 25.95 mA/cm² to 22.07 mA/cm² when the buffer thicknesses increase from 10 nm to 100 nm. While J_{sc} changes slightly if μc-3C-SiC is used as the buffer layer. This should be come from the fact that the optical absorption coefficient of μc-3C-SiC is rather low. If a-Si is used as the buffer layer of CZTS, the buffer layer should be not too thick. Fig. 3b depicts the influence of the buffer thickness on cell open-circuit voltage V_{oc} with CdS, a-Si and μc-3C-SiC buffer layers, respectively. It is found that the change of V_{oc} of the cell with μc-3C-SiC buffer layer is minimum. For the cell with a-Si buffer layer, V_{oc} decreases from 1.008 V to 0.982 V when the buffer thickness increases from 10 nm to 100 nm. It should be mentioned that V_{oc} increases or decreases logarithmically with the increasing or decreasing J_{sc} according to the formula [26]

$$V_{oc} = \frac{kT}{q} \left[\ln \left(\frac{J_{sc}}{J_0} \right) + 1 \right] \quad (8)$$

where k is the Boltzmann constant, T is the absolute temperature, q is the electron charge, and J_0 is the dark saturation current density. But here note that Eq. (8) is applicable for ideal solar cells, without taking into account the series or shunt resistance. For a real solar cell, the series resistance should be increased with the increase of the buffer thickness. This would cause a decrease in J_{sc} . In Fig. 3c, we plot the cell efficiency as a function of the buffer thickness with different buffer layers. It can be seen that the efficiency of the cell with μc-3C-SiC buffer has little change when the buffer thickness increases from 10 nm to 100 nm. But, that of the cell with a-Si buffer decreases rapidly from 21.45% to 14.79% when the buffer thickness increases from 10 nm to 100 nm. The big reduction of efficiency is due to the fact that the optical absorption coefficient of a-Si is very large and the mobility of it is very low. It can be seen from Fig. 2 that the sunlight is incident from the left side, pass the wide-bandgap ZnO window and buffer layer, and then reach the CZTS absorber. The solar photons absorbed by a-Si buffer cannot attribute to the light current.

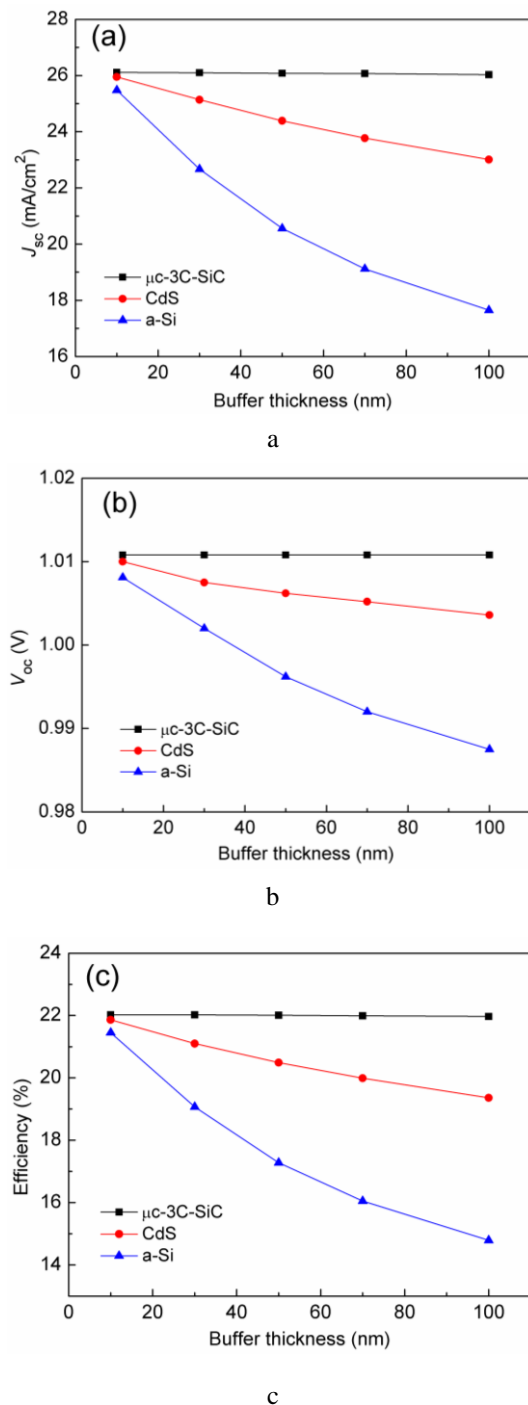


Fig. 3. Influence of the buffer thickness on short-circuit current density J_{sc} , open-circuit voltage V_{oc} and conversion efficiency with CdS, a-Si and $\mu\text{c-3C-SiC}$ buffer layers, respectively.

Fig. 4 shows the current-voltage curves for different thicknesses when the buffer layers are CdS, a-Si and $\mu\text{c-3C-SiC}$, respectively. It is found that the current-voltage curves almost overlap when the $\mu\text{c-3C-SiC}$ buffer increases from 10 nm to 100 nm. J_{sc} has significant deviation and V_{oc} change slightly when the thickness of CdS and a-Si buffers increases from 10

nm to 100 nm. In order to further investigate above-mentioned phenomenon, we calculate the quantum efficiency (QE) of the CZTS solar cells with $\mu\text{c-3C-SiC}$, a-Si and CdS buffers as shown in Fig. 5. It is found that the QE in the short-wavelength region gets worse when the buffer of CdS or a-Si increases. And little absorption loss is found in short-wavelength region for the cell with $\mu\text{c-3C-SiC}$ buffer. These results suggest that the blue light response of the CZTS solar cell is significantly improved by using $\mu\text{c-3C-SiC}$ buffer instead of a-Si or CdS buffer.

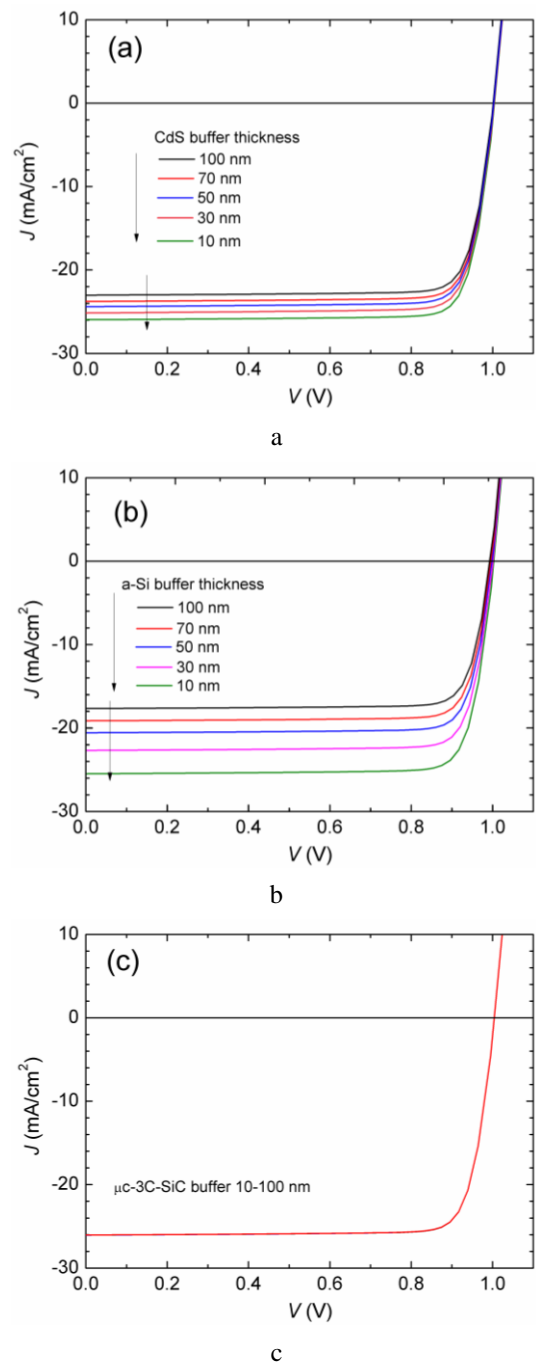


Fig. 4. Current-voltage curves for different thicknesses when the buffer layers are CdS, a-Si and $\mu\text{c-3C-SiC}$, respectively.

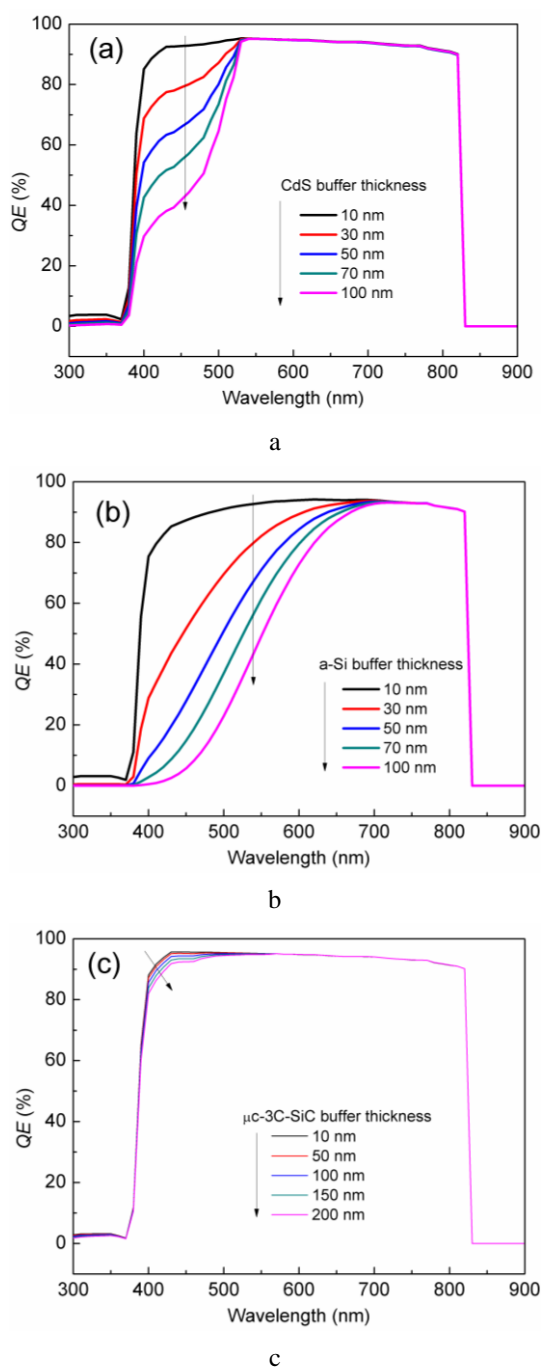


Fig. 5. QE curves of the CZTS solar cell with different buffer thicknesses using CdS, a-Si and $\mu\text{C-3C-SiC}$ buffers, respectively.

Fig. 6 illustrates the current-voltage curves of the CZTS solar cell with different densities of interface states when the buffer layer is a-Si. It is found that interface states have important impacts on cell performance. Obviously, interface states can make photocarriers recombined and result in the decrease in J_{sc} . Besides, high interface states can bring about a big dark saturation current density, which would deteriorate the open-circuit voltage. The addition of interface states is to study the effect of surface passivation on cell performance. It is

well known that a good passivation would reduce the interface states. The better the surface passivation is, the lower the density of interface states is. And amorphous or microcrystalline materials possess passivation property [27,28]. This is a unique advantage that uses as the buffer layer for the CZTS solar cell.

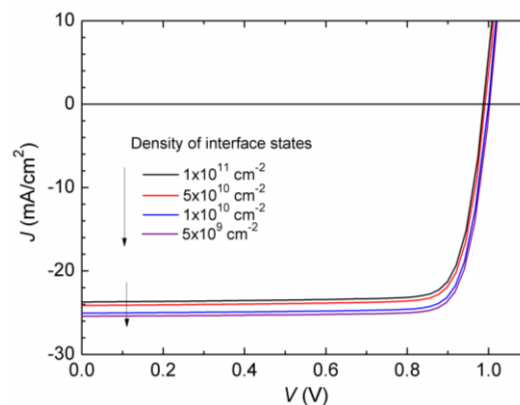


Fig. 6. Current-voltage curves for different densities of interface states when the buffer layer is a-Si.

4. Conclusions

We have studied the CZTS solar cells with a-Si or $\mu\text{C-3C-SiC}$ novel buffer layer. We found that using a-Si as buffer can result in large optical absorption loss in the short-wavelength region. The a-Si buffer layer should not be too thick for higher conversion efficiency. $\mu\text{C-3C-SiC}$ buffer can significantly improve the blue light response of the CZTS solar cell. Considering that $\mu\text{C-3C-SiC}$ and a-Si have passivation property and are CdS-free, they may be two promising materials for the buffer of CZTS solar cells.

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