Solar Energy 164 (2018) 231–242

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Analysis of the open-circuit voltage of $Cu_2ZnSn(S, Se)_4$ thin film solar cell

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ARTICLE INFO

Keywords:
CZTSSe thin film solar cell
Open-circuit voltage
Numerical analysis
Back surface field

ABSTRACT

Currently, the conversion efficiency of $Cu_2ZnSn(S, Se)_4$ (CZTSSe) thin film solar cell is mainly limited by its low open-circuit voltage. In this work, the performances of CZTSSe thin film solar cell were calculated by the simulation program AFORS-HET v2.5 to reveal some useful ways to enhance the open-circuit voltage. First, several factors affecting the open-circuit voltage were analyzed. The open-circuit voltage of CZTSSe solar cell was significantly improved by reducing the defect states, interface states, parasitic resistance effect, and formation of MoS_2 layer, and adjusting the hole concentration or band gap of CZTSSe absorber. Then, the band gap gradient was introduced into the CZTSSe absorber to extend the built-in electric field and enhance absorptions, leading to benign impacts on the open-circuit voltage of CZTSSe solar cell. Finally, a back surface field was considered for the CZTSSe solar cell. The effects of CZTSSe and amorphous silicon back surface fields depended on the defect states. The advantage of back surface field was prominent when the defect density was low. It was necessary to reduce the defects before considering a back surface field. In the calculations, the best CZTSSe solar cell had an open-circuit voltage deficit of only 0.134 V. The numerical analyses in this work provide some methods to improve the open-circuit voltage and conversion efficiency CZTSSe thin film solar cell. The proposed methods offer guidance for experimental works.

1. Introduction

Since 2010, the semiconducting compound $Cu_2ZnSn(S, Se)_4$ (CZTSSe) thin film solar cell has attracted world-wide attention as an alternative to traditional $Cu(In, Ga)Se_2$ photovoltaic cell that contains the rare element In (Huang et al., 2014; Ramasamy et al., 2012; Shi et al., 2017). All elements in the CZTSSe absorber are non-toxic, earth-abundant, and environment-friendly. The CZTSSe absorber has absorption coefficients of higher than $1 \times 10^4\ cm^{-1}$ in the visible light region and a direct optical band gap of 1.0–1.5 eV depending on the S/Se ratio (Amal et al., 2014; Wu et al., 2018; Xue et al., 2016). Its optical band gap can be adjusted to match the optimum for single-junction solar cell. Therefore, CZTSSe thin film solar cell is a good candidate for novel photovoltaic technology.

However, the reported conversion efficiency of CZTSSe thin film solar cell is far lower than that of $Cu(In, Ga)Se_2$ solar cell (Green et al., 2017; Todorov et al., 2012; Wang et al., 2014; Yan et al., 2017a). The champion CZTSSe thin film solar cell was fabricated by hydrazine solution method in 2014 (Wang et al., 2014). It has open-circuit voltage (V_{oc}) of 513.4 mV, short-circuit current density (J_{sc}) of 35.2 mA/cm^2, fill factor (*FF*) of 69.8%, and conversion efficiency (η) of 12.6%. The J_{sc} is close to the highest value determined by the band gap of absorber and illumination spectrum, but the V_{oc} is much lower than the limit value given by the band gap of absorber. The open-circuit voltage deficit ($E_g/q - V_{oc}$) is 616.6 mV, where E_g and q are the band gap of absorber and elementary charge, respectively. Other literatures also report large open-circuit voltage deficits (Hironiwa et al., 2015; Li et al., 2016; Miskin et al., 2015; Todorov et al., 2012; Yan et al., 2017a). The low V_{oc} limits the *FF* and η of solar cell. Therefore, V_{oc} is the main problem limiting the development of CZTSSe thin film solar cell.

Many studies have carried out experimental works to improve the V_{oc} of CZTSSe thin film solar cell by optimizing the fabrication process, doping the absorber, or adding a novel buffer layer (Feng et al., 2017; Kim et al., 2017; Yang et al., 2017; Zhao et al., 2017). Novel structures for CZTSSe absorber have also been designed. Yan et al. employed double Cu_2ZnSnS_4 layers with different carrier concentrations as an absorber to improve V_{oc} from 665 mV to 734 mV (Yan et al., 2017b). Tajima et al. used similar CZTS solar cell structure with carrier concentration gradient in the absorber, and reported the V_{oc} increased from 0.66 V to 0.78 V (Tajima et al., 2015). However, the reported improvements in V_{oc} are not notable as the V_{oc} values are far less than E_g/q.

Device simulation is a useful tool to study solar cells. The properties of a solar cell can be predicted using the numerical analysis of simulation program. There are simulation reports about CZTSSe solar cell in recent years. Several reports studied the influences of various layer

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https://doi.org/10.1016/j.solener.2018.02.066
Received 1 January 2018; Received in revised form 16 February 2018; Accepted 26 February 2018

parameters on the basic CZTSSe solar cell (Arbouz et al., 2017; Frisk et al., 2016; Meher et al., 2016; Xu and Yao, 2012). Different buffer layers (Cherouana and Labbani, 2017; Lin et al., 2016) and the band gap grading in the absorber (Adewoyin et al., 2017; Mohammadnejad and Parashkouh, 2017; Simya et al., 2016) have also been studied by simulation. However, scarce simulation work focused on the V_{oc} problem of CZTSSe solar cell. The highest calculated value of V_{oc} was 1.127 V which gave a V_{oc} deficit of 0.373 V (Xu and Yao, 2012).

In this work, we explored ways to improve the V_{oc} of CZTSSe thin film solar cell by numerical analysis. Several factors affecting the V_{oc}, such as the defect states in the absorber, the interface states, the parasitic resistances, the carrier concentration and band gap of absorber, and the formations of MoS_2 layer and secondary phases, were analyzed in detail. During calculations, the J_{sc} and η were also considered because the V_{oc} and J_{sc} may change conversely in certain cases. In addition, we considered some new designs of solar cell structure for improving V_{oc}. The effects of band gap gradient in CZTSSe absorber and back surface field (BSF) were calculated to determine their feasibility. The numerical analyses in this work are expected to provide guidance for future experimental works.

2. Calculation method

The numerical simulation program AFORS-HET v2.5, developed by Helmholtz-Zentrum Berlin (HZB) (Varache et al., 2015), was utilized for the calculations. The basic structure of CZTSSe solar cell was ZnO:Al/ZnO/CdS/CZTSSe as shown in Fig. 1. The illumination entered from the ZnO:Al side. For the calculations of new design solar cell, two conditions were considered: a band gap gradient was employed to the CZTSSe absorber, and a BSF layer was inserted between the absorber and back electrode. The input physical parameters of each layer were obtained from literature (Cherouana and Labbani, 2017; Frisk et al., 2016; Kanevce et al., 2015; Wang et al., 2014; Xu, 2016; Xu and Yao, 2012) and summarized in Table 1. The hole concentration and band gap of CZTSSe were changed in reasonable range to study their impacts. For the bulk defect states in CZTSSe, the acceptor and donor defects were gauss type and located at mid-gap, and the neutral defects were single and mid-gap (Frisk et al., 2016; Xu, 2016). The acceptor and donor defects in the CdS/CZTSSe interface were located at mid-gap. The serial and shunt resistances of solar cell were also considered. The Lambert–Beer model was utilized as the optical model. The incident light spectrum was standard AM 1.5.

The properties of CZTSSe solar cell were obtained by numerical solution of the basic semiconductor equations including Poisson's equation, continuity equation, and current equations of carriers. In the new version of AFORS-HET program, the carrier tunneling through spikes in the energy band discontinuity and trap-assisted tunneling in bulk materials were concerned for more accurate calculations. The thermal equilibrium properties of solar cell, such as the band diagrams, carrier concentration distribution, and carrier recombination, could be obtained. Under illumination, the photovoltaic parameters (V_{oc}, J_{sc}, *FF*, and η), current–voltage (*I–V*) curve, and spectral response could be calculated. In this work, we focused on the V_{oc} and η of solar cell.

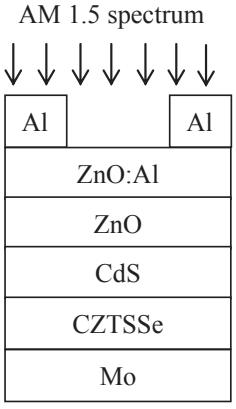

Fig. 1. The basic structure of CZTSSe thin film solar cell used in the calculation.

Table 1
The physical parameters of each layer in the simulated CZTSSe thin film solar cell.

Material properties	ZnO:Al	ZnO	CdS	CZTSSe
Thickness (nm)	200	50	50	2000
Dielectric permittivity	10	10	9	10
Electron affinity (eV)	4.4	4.4	4.5	4.5
Band gap (eV)	3.4	3.4	2.4	Variable
Conduction band effective density of states (cm^{-3})	2×10^{18}	2×10^{18}	1.8×10^{19}	2×10^{18}
Valence band effective density of states (cm^{-3})	2×10^{18}	2×10^{18}	2.4×10^{18}	2×10^{18}
Electron mobility ($cm^2/(V{\cdot}s)$)	20	20	350	40
Hole mobility ($cm^2/(V{\cdot}s)$)	20	20	50	10
Electron concentration (cm^{-3})	1×10^{20}	–	1×10^{17}	–
Hole concentration (cm^{-3})	–	–	–	Variable
Electron thermal velocity (cm/s)	1×10^{7}	1×10^{7}	1×10^{7}	1×10^{7}
Hole thermal velocity (cm/s)	1×10^{7}	1×10^{7}	1×10^{7}	1×10^{7}

In the calculation, we first fitted the photovoltaic properties of CZTSSe solar cell to the reported champion cell (Wang et al., 2014). Then, the changes of photovoltaic properties with defect states, parasitic resistances, hole concentration and band gap of absorber, and the formation of MoS_2 layer were calculated. Furthermore, we considered the effects of band gap gradient in CZTSSe absorber and adding a BSF layer on the V_{oc} and η of solar cells.

3. Results and discussion

3.1. The basic CZTSSe thin film solar cell

First, we build a basic CZTSSe thin film solar cell (reference cell) based on the reported champion CZTSSe cell. The champion cell has absorber with band gap of 1.13 eV and thickness of 2 μm, series resistance of 0.72 Ω·cm^2, and shunt resistance of 621 Ω·cm^2 (Wang et al., 2014). In the simulation, we adjust the hole concentration of CZTSSe and defect densities in the CZTSSe layer and CZTSSe/CdS interface to get the calculated results near the reported cell. After fitting, the hole concentration of CZTSSe is set to 1.4×10^{16} cm^{-3}. The densities of acceptor, donor, and neutral defects in CZTSSe are 1×10^{16} cm^{-3}, 1×10^{16} cm^{-3}, and 3.9×10^{16} cm^{-3}, respectively. The density of interface defects is 1×10^{16} cm^{-2}. The reference cell has photovoltaic properties of $V_{oc} = 0.513$ V, $J_{sc} = 36.5$ mA/cm^2, $FF = 60.84\%$, and $\eta = 11.39\%$. The calculated V_{oc} is equal to that of the champion cell. However, the other three parameters have tiny differences with those of the champion cell due to the limit of device model used in the simulation.

3.2. The effect of defect states

According to the single-diode model, the current density–voltage (*J–V*) relation of solar cell is given by

$$J = J_{ph} - J_0\left[\exp\left(\frac{qV}{nkT}\right) - 1\right], \quad (1)$$

where J_{ph}, J_0, n, k, and T are the photo-generated current density, reverse saturation current density, ideality factor, Boltzmann's constant, and absolute temperature, respectively. According to Eq. (1), by setting $J = 0$, the V_{oc} of solar cell can be obtained as

$$V_{oc} = \frac{nkT}{q}\ln\left(\frac{J_{ph}}{J_0} + 1\right). \quad (2)$$