

The Influence of Conduction Band Offset on CdTe Solar Cells

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Numerical modeling of conduction band offset ($\Delta E_{\rm C}$) between an *n*-type CdSO window layer and a *p*-type CdTe absorption layer on the effect of the cadmium telluride (CdTe) solar cells was studied through simulation. The simulation results show that a slightly positive $\Delta E_{\rm C}$ yields high efficiency because the surface recombination rate at the CdSO/CdTe interface can be substantially reduced, leading to higher open-circuit voltage ($V_{\rm OC}$) and fill factor. Further increase in $\Delta E_{\rm C}$ (\geq 0.4 eV) will impose an energy barrier against the photogenerated electrons under forward bias. We demonstrated the mechanistic picture of this effect using thermionic emission. However, if intra-band tunneling is considered in the simulation, a large $\Delta E_{\rm C}$ shows negligible influence on the performance of CdTe solar cells. Our simulation results suggest that an $\Delta E_{\rm C}$ of 0.3 eV is an optimal conduction band offset for high-efficiency CdTe solar cells.

Key words: CdTe solar cell, conduction band offset, surface recombination rate, thermionic emission, intra-band tunneling

INTRODUCTION

The cadmium telluride (CdTe) solar cell is one of the three major branches in thin film technologies. Since the band gap of CdTe thin film is 1.5 eV, it has a great potential to yield a high conversion efficiency (η) solar cell, as seen from the Shockley-Queisser diagram.¹ The typical superstrate configuration of CdTe solar cells is comprised of a glass superstrate, a transparent conductive oxide (TCO) layer, a cadmium sulfide (CdS) *n*-window layer, a CdTe absorber layer, a Cu back contact and a metal electrode. Despite the great potential for high efficiency, there are two main limiting factors. The first is the low doping concentration in CdTe, which is usually no higher than 10^{15} cm⁻³. Different techniques have already been tried by some researchers in order to increase the doping

concentration of CdTe, such as doping Cu in Terich CdTe and doping P or As in Cd-rich CdTe.² The second is the blue loss that originates from the low band gap of CdS. Incident light with a photon energy greater than 2.45 eV will not contribute to the quantum response of CdTe solar cells, which can significantly reduce the short-circuit current (J_{SC}) . Furthermore, the efficiency (η) of CdTe solar cells can be enhanced by 2.3% once the blue loss is removed.⁵ Some researchers have also reported that the wider band gap n-window layer can increase not only $J_{\rm SC}$ of CdTe solar cells but also the open-circuit voltage (V_{OC}) and fill factor (FF).^{6,7} So, studying and utilizing the wider band gap semiconductor film as the *n*-window layer is the key for high-efficiency CdTe thin film solar cells.

Cadmium sulfide oxide (CdSO) is one of the important wider band gap *n*-window candidates. The group led by Wu first introduced this material into CdTe solar cells through their publications in the early 2000s.⁸ They synthesized CdSO samples with different oxygen content by carrying out

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deposition at different oxygen/argon (O/Ar) ratios. The band gap of CdSO samples could then be controlled and a series of CdTe solar cells with a structure of CTO/ZTO/CdSO/CdTe were fabricated. The performance of their fabricated solar cells is much better than others made by CdS as the nwindow layer. In 2014, researchers from the Colorado School of Mines then concluded that amorphous CdSO layers with an optical band gap of 2.8 eV and 45% O result in the highest observed efficiency. Duncan, from the University of Nevada, together with other researchers, published a paper on the material analysis for CdSO in 2015.¹⁰ The results showed that CdSO films were mainly comprised of CdS and CdSO₄, with small additions of an intermediate CdSO_x (most likely sulfite) species. CdSO₄ is the preferred species when oxygen incorporation is increasing, whereas the content of the intermediate oxide species remains constant. Further investigation on CdSO was carried out by a research group in Colorado State University through a publication in 2015.¹¹ They ascribed the increase of the band gap of CdSO to the alloying of high band gap sulfate and sulfite with CdS. Experimental results indicated that the optimized range for the ratio Ar/O₂ during the deposition of CdSO was 1.5– 2.5%.

Once CdSO is used as the *n*-window layer, blue loss is largely removed and so $J_{\rm SC}$ will be enhanced. The increase of $V_{\rm OC}$ and FF should be ascribed to the change of $\Delta E_{\rm C}$. From Anderson's law, the value of $\Delta E_{\rm C}$ here is defined as

$$\Delta E_{\rm C} = \chi_{\rm absorber} - \chi_{n-\rm window} \tag{1}$$

Different materials have different electron affinity. Since the value of $\Delta E_{\rm C}$ is only determined by the materials that form the heterojuction, the value of $\Delta E_{\rm C}$ will change if the new *n*-window material is applied. Minemoto's group first discussed the influence of $\Delta E_{\rm C}$ on the performance of CIGS solar cells. They concluded that the highest efficiency can be achieved when $\Delta E_{\rm C}$ is between 0 eV and 0.4 eV.¹² In our previous work, the influence of $\Delta E_{\rm C}$ on CdTe solar cells was briefly discussed, and the optimized $\Delta E_{\rm C}$ obtained by numerical simulations was in the range of 0.1 eV to 0.3 eV.¹³ However, the accuracy and reliability of the simulated results can be improved by either changing some of the input parameters or by taking more mechanisms into consideration, for example, thermionic emission and intra-band tunneling. In addition, deep theoretical analysis on the results is not provided in the previous work, thus the influence of $\Delta E_{\rm C}$ on the performance of CdTe solar cells still has to be further investigated and explained.

In this paper, systematic computer simulation was used to investigate the influence of $\Delta E_{\rm C}$ between the CdTe absorber layer and the *n*-window layer on the performance of CdTe solar cells. CdSO was the material chosen as the *n*-window layer in the simulation. The $V_{\rm OC}$, $J_{\rm SC}$, FF and η of the simulated cell were plotted as a function, $\Delta E_{\rm C}$. Two different conditions are considered here as to whether or not intra-band tunneling is included. It can be expected that the performance of CdTe under these two conditions will be quite different.

METHODS

CdSO thin films were deposited on TCO glass substrates, and the oxygen content in the CdSO thin films was controlled by turning the O/Ar ratio from 0% to 6%. The samples' transmittance spectrum was measured by a violet–visible–near infrared (UV– Visible-NIR) spectrometer. The band gap of the sample was calculated by performing a Tauc plot of the measured transmittance data. All optical properties of the samples are shown in Fig. 1. The data for CdSO sample with O/Ar ratio of 5% was chosen as the input parameters for the simulation. The thickness of the sample was 70 nm, the doping concentration of the sample was assumed to be 10^{16} cm⁻³, and the band gap of the sample was 3.2 eV achieved from Fig. 1b.

As a one-dimension simulation program, solar cell capacitance simulator (SCAPS) is commonly used to numerically simulate the performance of solar cells.¹⁴ The program can build different kinds of solar cell devices by setting up different layers and



Fig. 1. The optical properties of the measured CdSO samples. (a) The transmittance of CdSO samples in terms of wavelength. (b) The Tauc plot of the measured samples.

Table I. The initial parameters of each layer of the simulated solar cell

Layer	TCO	CdSO	CdS	Interface	<i>p</i> -CdTe
Thickness (nm)	500	70	70		2500
Band gap (eV)	3.7	3.2	2.42	_	1.5
Electron affinity (eV)	4.5	4.5	4.5	_	4.4
Relative dielectric permittivity	10	10	10	_	9.4
Density states of conduction band (cm^{-3})	$2.2 imes10^{18}$	$2.2 imes10^{18}$	$2.2 imes10^{18}$	_	$8.0 imes 10^{17}$
Density states of valence band (cm^{-3})	$1.8 imes10^{19}$	$1.8 imes10^{19}$	$1.8 imes10^{19}$	_	$1.8 imes10^{19}$
Electron mobility $(cm^2/V s)$	32	100	100	_	320
Hole mobility $(cm^2/V s)$	30	25	25	_	40
Donor concentration (cm ⁻³)	$1.0 imes10^{19}$	$1.0 imes10^{16}$	$1.0 imes10^{16}$	_	_
Acceptor concentration (cm^{-3})	_	-	_	_	$1.0 imes10^{15}$
Dopant energy level (eV)	_	0.14	0.14	-	0.255
Defect type	SA	SA	SA	Ν	\mathbf{SD}
Electron cross-section (cm^{-2})	$1.0 imes10^{-15}$	$1.0 imes10^{-17}$	$1.0 imes10^{-17}$	$1.0 imes10^{-15}$	$1.0 imes10^{-13}$
Hole cross-section (cm^{-2})	$1.0 imes10^{-12}$	$1.0 imes10^{-12}$	$1.0 imes10^{-12}$	$1.0 imes10^{-15}$	$1.0 imes10^{-15}$
Defect concentration (cm^{-2})	$1.0 imes10^{16}$	$3.0 imes10^{15}$	$3.0 imes10^{15}$	$1.0 imes10^{13}$	$2.0 imes10^{13}$
Defect energy level (eV)	2.0	1.9	1.12	0.6	0.585

interfaces between them. Then, it numerically solves Poisson and continuity equations for electrons and holes in one dimension to determine the band diagram of the solar cell devices and their response to illumination, voltage bias and temperature. After that, the performance of the solar cells is simulated by the program, such as J–V, C–V and QE.

In this simulation, a CdTe solar cell was built with the following order: back contact, CdTe, (Interface), CdSO, TCO, and front contact. A comparison solar cell using CdS to replace CdSO as the *n*window layer was also simulated. To discover the influence of the band gap of the *n*-window layer, most of the parameters were kept the same between CdSO and CdS. The major difference between the two different *n*-window layers is the value of the band gap. For CdSO, the band gap was 3.2 eV, while for CdS, the band gap was 2.42 eV. Initial parameters of the simulation were partly taken from other papers.^{11,15,16} Then, J–V and QE simulations were run on both cells and the results were compared to show the removal of the blue loss.

After that, the influence of $\Delta E_{\rm C}$ on the performance of CdTe solar cells was determined by inputting different values on the electron affinity of CdSO. There should be some relationship between the band gap and the electron affinity of CdSO with the variation of O content in real samples, but here we kept the band gap of CdSO the same in order to investigate the influence of $\Delta E_{\rm C}$ individually. Performance calculations were made using simulated J–V sweeps in the simulation under illumination by the AM 1.5 G spectrum at 100 mW/cm² of intensity and 300 K. The plot of the $V_{\rm OC}$, $J_{\rm SC}$, FF, η of CdTe solar cells as a function of $\Delta E_{\rm C}$ are displayed in Fig. 3 (Table I).



Fig. 2. Simulated QE results of two different CdTe solar cells with CdSO and CdS as the *n*-window layer, respectively.

RESULTS AND DISCUSSION

The Influence of Band Gap of the *n*-Window Layer

Figure 2 depicts the QE results of two different CdTe solar cells with CdSO and CdS as the *n*-window layer, respectively. The results clearly demonstrate that the blue loss can be largely removed, as expected. To show the influence of the removal of the blue loss individually, $\Delta E_{\rm C}$ was kept the same at -0.1 eV. The simulated J–V results are also shown in Fig. 2. $J_{\rm SC}$ increases drastically but $V_{\rm OC}$ and FF remain mostly constant after the blue loss is removed. The efficiency of the solar cell only increases by 0.83%, which is smaller than observed in other researchers' experimental data. This means there is still potential to improve the efficiency of CdTe solar cells by increasing $V_{\rm OC}$ and FF by adjusting $\Delta E_{\rm C}$ between CdSO/CdTe layers.

The Influence of $\Delta E_{\rm C}$ Between CdSO/CdTe Layers

Figure 3 shows the $V_{\rm OC}$, $J_{\rm SC}$. FF and η of the simulated solar cells as a function of $\Delta E_{\rm C}$ from -0.3 eV to +0.7 eV. The simulation was run for conditions with and without intra-band tunneling.

The $V_{\rm OC}$ of CdTe solar cells as a function of $\Delta E_{\rm C}$ is almost the same in cases with and without intraband tunneling. $V_{\rm OC}$ first increases dramatically with $\Delta E_{\rm C}$ when $\Delta E_{\rm C}$ is negative. However, the increase of $V_{\rm OC}$ slows down when $\Delta E_{\rm C}$ becomes positive. The reduction of the surface recombination rate at the CdSO/CdTe interface is the main reason for this dramatic increase. Using the Shockley– Read–Hall model, the surface recombination rate (R) can be expressed as follows:

$$R = \frac{np - n_i^2}{S_n^{-1}(n + n^*) + S_n^{-1}(p + p^*)}$$
(2)

In this model, p is the nonequilibrium concentration for holes and n is the nonequilibrium concentration for electrons at the interface. n_i is the intrinsic concentration for the CdTe absorber. S_p and S_n are the surface recombination velocities for holes and electrons, respectively. The quantities p^* and n^* are defined as follows:

$$p^* = N_{\rm V} \exp[-(E_{\rm D} - E_{\rm V})/kT] \qquad (3)$$

$$n^* = N_{\rm C} \exp[-(E_{\rm C} - E_{\rm D})/kT] \tag{4}$$

In these equations, $N_{\rm V}$ and $N_{\rm C}$ are the effective density states in the valence band and conduction band for CdTe absorber, respectively. $E_{\rm D}$ is the defect energy level at the interface. $E_{\rm V}$ and $E_{\rm C}$ are the energy level for the valence and conduction bands, respectively. k is the Boltzmann constant, which is equal to $1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$. T is the temperature. The whole term kT is equal to 0.026 eV at normal temperature (300 K).

In this case, at the interface of the CdSO and the CdTe layers, n is much larger than p, p^* , and n^* , and np is much larger n_i^2 in nonequilibrium conditions. Since $S_p = S_n = 10^5$ cm s⁻¹ is set here, Eq. 2 can be simplified as follows:

$$\mathbf{R} = S_p p \tag{5}$$

The concentration of holes from the CdTe absorber side at the interface dominates the surface recombination rate. So, p can be expressed as follows:



Fig. 3. Simulated performance of CdTe solar cell as a function of $\Delta E_{\rm C}$. (a) $V_{\rm OC}$ as a function of $\Delta E_{\rm C}$. (b) $J_{\rm SC}$ as a function of $\Delta E_{\rm C}$. (c) FF as a function of $\Delta E_{\rm C}$. (d) Efficiency as a function of $\Delta E_{\rm C}$.



Fig. 4. Simulated band diagram of CdTe solar cells at different $\Delta E_{\rm C}$ with band bending enlarged. (a) $\Delta E_{\rm C} = -0.2$ eV. (b) $\Delta E_{\rm C} = 0$ eV. (c) $\Delta E_{\rm C} = 0.2$ eV.

$$p = N_{\rm V} \exp(-E_p/kT) \tag{6}$$

Here, $E_{\rm p}$ is called the "hole barrier" and can be expressed as follows:

$$E_p = BB + \Delta E_p \tag{7}$$

Here, BB indicates the band bending, and ΔE_p is defined as the distance between the quasi-Fermi level for holes (E_{Fp}) and the conduction band energy level of the CdTe absorber layer. The expression for ΔE_p deduced from Maxwell–Boltzmann's distribution equation is as follows:

$$\Delta E_p \simeq -kT \ln\left(\frac{N_{\rm A}}{N_{\rm V}}\right) \tag{8}$$

Here, $N_{\rm A}$ indicates the doping concentration of the CdTe absorber, and is a constant for 10^{15} cm⁻³. Thus, E_p is mainly dominated by band bending.

Figure 4 shows three simulated band diagrams at three different values of $\Delta E_{\rm C}$ (-0.2 eV, 0 eV, 0.2 eV) with band bending emphasized. The results show that band bending increases with $\Delta E_{\rm C}$. So, pwill decrease and the surface recombination rate will also decrease with the increase of $\Delta E_{\rm C}$. The decrease of the surface recombination rate means a longer carrier lifetime for holes (τ_p) and electrons (τ_n). This will decrease the saturation or dark current density (J_0), which in this case can be expressed as:

$$J_0 \propto \frac{q n_i W}{\tau_n} \tag{9}$$

where q is the charge of an electron, which equals 1.6×10^{-19} C. W is the width of the depletion region, which is mainly determined by the doping concentration of the layers that form the diode, and is independent of $\Delta E_{\rm C}$. $V_{\rm OC}$ is related to J_0 as follows:

$$V_{\rm OC} = \frac{AKT}{q} \ln\left(\frac{J_{\rm SC}}{J_0}\right) \tag{10}$$

Here, A is the diode quality factor. Since J_0 decreases when $\Delta E_{\rm C}$ increases, from the equation above, $V_{\rm OC}$ can be improved by increasing $\Delta E_{\rm C}$, as we see from the simulated results, because it is reverse proportional to J_0 .

However, $V_{\rm OC}$ cannot increase indefinitely, as it has an upper limit. In this study, an empirical equation was proposed which establishes a relationship between the upper limit of $V_{\rm OC}$ and built-in voltage ($V_{\rm bi}$).

$$V_{\rm OC} \le V_{\rm bi} = \frac{1}{q} \left(E_{gp} + \Delta E_{\rm C} - \Delta E_n - \Delta E_p \right) \qquad (11)$$

The flat band diagram of a typical CdTe solar cell with CdS as *n*-window layer is shown in Fig. 5a. All the symbols and their approximate values in Eq. 11 are listed in the figure. For the traditional CdTe



solar cells, the upper limit of $V_{\rm OC}$ is 1.0 eV, but it can also be increased with $\Delta E_{\rm C}$ when wider band gap *n*-window material is used. However, this equation cannot always be right when $\Delta E_{\rm C}$ becomes positive and continues increasing. The reason is that the quasi-Fermi level splitting is impossible to be more than the CdTe absorber band gap, and the Fermi level of CdSO will be effectively pinned at or below the CdTe absorber conduction band when $\Delta E_{\rm C}$ is the 'spike' case, as shown in Fig. 5b. Then, $V_{\rm OC}$, as well as $V_{\rm bi}$, can only increase slightly, but no longer linearly with $\Delta E_{\rm C}$, which meets the simulated results.

The Influence of $\Delta E_{\rm C}$ on $J_{\rm SC}$

 $J_{\rm SC}$ remains almost constant when $\Delta E_{\rm C}$ is smaller than 0.4 eV in cases with and without intra-band tunneling. The reason is that, when $\Delta E_{\rm C}$ is negative, there is no barrier against the photo-generated current. Therefore, $J_{\rm SC}$ is mainly determined by the band gap of CdTe and is independent of $\Delta E_{\rm C}$. However, when $\Delta E_{\rm C}$ becomes positive, it will act as a 'spike' which impedes the photo-generated current, as shown in Fig. 4c. So, the thermionic emission is used for the photo-generated electrons to climb through the 'spike.' The thermionic emission current density ($J_{\rm TE}$) can be approximately calculated using the following equation,

$$J_{\rm TE} = A^* T^2 \exp(-q\phi_B/kT) \tag{12}$$

where A^* is the Richardson constant, which is equal to:

$$A^* = \frac{4\pi m^* k^2}{h^3}$$
(13)

where m° is the effective mass of an electron in the CdTe absorber, which is equal to $0.11m_0$, or 1.0×10^{-32} kg. *h* is the Planck constant, which equals 6.63×10^{-34} J.s.

 ϕ_B is the barrier height for electrons. Theoretically speaking, ϕ_B is the distance between the maximum point of $E_{\rm C}$ at the interface and the quasi-Fermi level for electrons (E_{Fn}) of CdTe absorber. In this case, we can regard ΔE_{C} as ϕ_B since the difference between them is negligible. Putting the value of all the parameters into the two equations above, we can find the calculated J_{TE} will be extremely small when $\Delta E_{\rm C}$ is larger than 0.5 eV. This is the reason that $J_{\rm SC}$ starts to decline after $\Delta E_{\rm C}$ reaches 0.4 eV if intra-band tunneling is not included. Finally, the cell will fail to work if $\Delta E_{\rm C}$ is too large. However, if intra-band tunneling is included, the electrons can tunnel through the barrier and $J_{\rm SC}$ will not decrease even after it reaches 0.5 eV. The model for the intraband tunneling applied in SCAPS is discussed by a paper published by researchers from the University of Gent.¹⁷ In their model, two important parameters, which can significantly influence the possibility of intra-band tunneling, are the height and width of the 'spike' when $\Delta E_{\rm C}$ is positive. The height of the 'spike', as discussed previously, is determined by the electron affinity of CdSO. The width of the 'spike' should be determined by the doping concentration of CdSO. It can be expected that a higher doping concentration of CdSO can minimize the width of the 'spike' and increase the possibility of intra-band tunneling. Here, the doping concentration for CdSO and CdS simulations are always set to be the same, at 10^{16} cm⁻³. Then, the width of the 'spike' should be the same, but the height of the 'spike' changes because of the difference in $\Delta E_{\rm C}$. It can be derived from the results that the intra-band tunneling can occur in all the simulated cases.

The Influence of $\Delta E_{\rm C}$ on Fill Factor

FF is mainly dependent on the series resistance of CdTe solar cells. It increases dramatically as the value of $V_{\rm OC}$ increases when $\Delta E_{\rm C}$ is below 0.2 eV. This is also due to the decrease of the surface recombination rate and increase of the carrier lifetime. However, if $\Delta E_{\rm C}$ is too large, the 'spike' will increase the series resistance of the CdTe solar cell. FF will decrease if intra-band tunneling is not included. It will not decrease if intra-band tunneling occurs because the 'spike' is not a resistance to the photo-generated current anymore.

An Optimized Structure for CdTe Solar Cells

The influence of $\Delta E_{\rm C}$ on the $J_{\rm SC}$, $V_{\rm OC}$, and FF of CdTe solars has already been mentioned. The efficiency of a solar cell is defined as

$$\eta = V_{\rm OC} * J_{\rm SC} * FF/P_{\rm income} \tag{14}$$

If intra-band tunneling occurs, the efficiency of the CdTe solar cell will increase with $\Delta E_{\rm C}$, mainly because of the increase of $V_{\rm OC}$ and FF. If intra-band tunneling does not occur, there is competition between the increase of $V_{\rm OC}$ and the decrease of $J_{\rm SC}$ when $\Delta E_{\rm C}$ is

increasing. The efficiency of the CdTe solar cell will increase with $\Delta E_{\rm C}$ at first, but decrease later and finally lead to the failure of the solar cell.

Although the intra-band tunneling can occur in all the simulated cases, to ensure the solar cells can perform well, a positive $\Delta E_{\rm C}$ with a value of 0.3 eV is highly recommended. Figure 5b shows the flat band diagram of the optimized structure of CdTe solar cells using CdSO as the *n*-window layer when $\Delta E_{\rm C}$ is 0.3 eV.

CONCLUSION

Using a new wider band gap material, CdSO as an example, to replace the traditional CdS as the *n*-window layer can help remove the blue loss of CdTe solar cells. Besides the increase of $J_{\rm SC}$, adjusting $\Delta E_{\rm C}$ by using a new *n*-window material can further enhance V_{OC} and FF of CdTe solar cells. Simulation results show that a slightly positive $\Delta E_{\rm C}$ yields high efficiency because the surface recombination rate at the interface can be substantially reduced. Further increase in $\Delta E_{\rm C}$ ($\geq 0.4 \text{ eV}$) will impose an energy barrier against the photo-generated electrons. The thermionic emission current density will then be extremely small and the CdTe solar cell will start to degrade. However, if the intraband tunneling is included in the simulation, the large $\Delta E_{\rm C}$ shows negligible influence on the performance of the CdTe solar cell. The simulated results suggest that $\Delta E_{\rm C}$ with a value of 0.3 eV may be an optimal conduction band offset for CdTe solar cells.

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