

NUMERICAL INVESTIGATIONS ON THE WORKING MECHANISMS OF SOLAR CELLS WITH A CdTe-BASED COMPOSITE-ABSORBER LAYER

X. YIN, L. WU*

Institute of Solar Energy Materials and Devices, College of Materials Science and Engineering, Sichuan University, Chengdu 610064, China

We investigated the working mechanisms of CdTe solar cells in which a second absorber-layer (defined as A2) with a lower bandgap was added through SCAPS simulation. The results show various positions and bandgap values of A2 are applicable at particular parameters, and the details are analyzed. We explored the essence of the improved cell performances via adding A2 for different occasions and provided some principles and models. Some new cognition for real cells was also presented. Additionally, we studied how the parameters of the wider-gap first absorber-layer influence the cell performances and its function as a back highly-resistant layer.

(Received May 16, 2020; Accepted September 5, 2020)

Keywords: CdTe solar cells; Composite absorber; Fermi level offset; Conduction band offset; Carrier lifetime; SCAPS simulation

1. Introduction

Recent progress in CdTe solar cells is mostly in the improved current density, realizing by application of wide-bandgap $Zn_xMg_{1-x}O$ as buffer layer and introduction of selenium to lower the bandgap of CdTe to extend the spectral response for photons with wavelength longer than $\sim 830\text{nm}$ [1-7]. For long-wave spectral response, it has been found in previous study that ternary layers like CdS_xTe_{1-x} formed through CdS/CdTe inter-diffusion show bowing phenomenon in the bandgap notwithstanding only several nanometers of the lower-gap CdS_xTe_{1-x} were observed in the entire device, contributing to negligible increasing in QE in the long-wave range and thus slightly increased current density [8-10]. $CdSe_xTe_{1-x}$ layer seems to augment this effect and it has been widely observed and acknowledged that using ternary $CdSe_xTe_{1-x}$ layer helps to maintain the Voc while increasing the Jsc. These results inspire us that if it is possible to improve the power conversion efficiency of CdTe solar cells by adding a second absorber with a lower bandgap to absorb more photons. Nevertheless, some questions still exist. For examples, is a composite structure or grading really that helpful? Can a material with even smaller bandgap than $CdSe_xTe_{1-x}$ be applied as a second absorber layer for CdTe solar cells and what are the underlining mechanisms? Thus, it's meaningful to give a discussion although the concept of the composite-absorber structure hasn't yet been extensively mentioned. Since a graded layer can be regarded as an infinite composite of materials with different energy gaps, it is able to speculate that it has similar properties with the two-absorber layer structure using the generalization method. Therefore, composite structures with two absorber layers can reflect some of the fundamental properties and will be discussed in detail in this communication.

*Corresponding authors: wulili@scu.edu.cn

Previous research for composite structures like $\text{CdSe}_x\text{Te}_{1-x}/\text{CdTe}$ stack focused on the preparation of such a graded structure and on the function of selenium, like passivating the defects at both grain boundaries and interiors[11~14], and there are few systematical related studies on solar cells with a composite-absorber structure by simulation for discussing the carrier generation and transportation mechanisms. In this work, the properties of composite-absorber structures with one absorber layer of pure-CdTe and another lower-gap one (defined as A2) were thoroughly investigated via theoretical analyses and SCAPS simulations to discover the underlying working mechanisms. This work aims to find out how a second absorber layer added into CdTe solar cells modifies the cell performances and the functions of the wide-gap absorber layer.

2. Modeling

Two cell structures for simulation were designed, as shown in Fig. 1. One structure is shown as Ideal Front Contact (Ideal FC)/Absorber 1(A1)/ Absorber 2(A2)/Ideal Back Contact (Ideal BC), defined as a Forward Structure (FS), and another is Ideal FC/A2/A1/Ideal BC, defined as a Reverse Structure (RS).

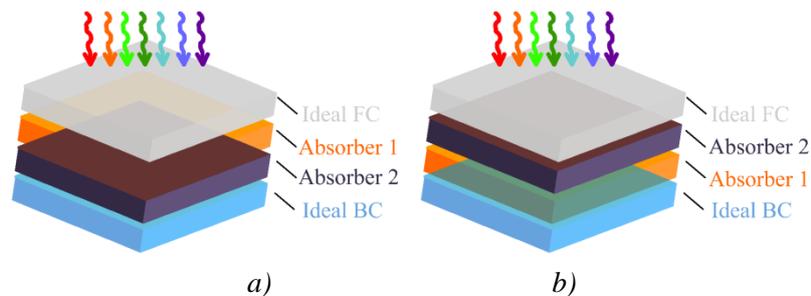


Fig. 1. Cell structures designed for simulation: (a) Forward Structure; (b) Reverse Structure. A1/A2 positions are different in different structures.

In this work, Absorber 1 (A1) represents CdTe ($E_g=1.5\text{eV}$) unless otherwise stated, while Absorber 2 (A2) has a smaller variable bandgap value between 1.2~1.4eV. Defect parameters are also designed and simply presented by minority carrier lifetime. Front and back contact layers are optimized to be ideal contacts based on our pre-simulation and some band alignment principles presented by others [15~17]. Some actual materials like $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ [17], Tellurium[18] seem to be helpful for forming such ideal contacts. Other main parameters of the materials involved in the simulation are given in Table 1.

Table 1. Major parameters of various functional layers used in the simulation.

Device Parameters	<i>n-FC</i>	<i>P-CdTe</i>	<i>P-Absorber 2</i>	<i>p-BC</i>
Thickness(<i>um</i>)	0.2	2	0~2	0.2
Bandgap(<i>eV</i>)	4.0	1.5	1.2~1.4	3
Affinity(<i>eV</i>)	optimized	4.3	4.0~4.6	optimized
Carrier concentration(<i>cm⁻³</i>)	10 ²⁰	~10 ^{13~16}	~10 ^{13~16}	10 ²⁰
Mobility(<i>cm/s</i>)	40/10	320/40	320/40	40/10
Defect Parameters				
Energy distribution	Mid-gap	Mid-gap	Mid-gap	Mid-gap
concentration(<i>cm⁻³</i>)	10 ¹⁹	10 ^{12~14}	10 ^{12~14}	10 ¹⁹
Minority Lifetime(<i>ns</i>)	0.001	1~100	1~100	0.001

Some other important material parameters like coefficient values are designed analogous to actual materials for relatively accurate simulation. All the photon losses due to reflection, interference at the surface and interface are neglected. As simulations are barely based on numerical values, the results can be extended to other solar cell systems with similar values. SCAPS3307 was used to simulate the cell performances. This software was developed and supported by Dr. Marc Burgelman from Ghent University. The main theoretical equations used for calculation are the Poisson Equation, electron and hole continuity equations, which have been described extensively in a lot of literature [19~22].

3. Results and discussion

3.1. The role of the second absorber layer

It is essential to know firstly the essence for the increased efficiency, namely, in what cases can the second absorber layer added improves the cell efficiency. CdSe_xTe_{1-x}&CdTe is the most typical case of the composite absorber structures and the simulation starts from this structure. Nevertheless, it is not enough to acquire comprehensive cognition by just discussing this case. In the following, we considered two kinds of combinations of the absorber layers, one with a small bandgap difference (1.4eV&1.5eV, like CdSe_xTe_{1-x}&CdTe), another with a relatively larger bandgap difference (1.2eV&1.5eV). Both cases will be simulated according to Fig. 1(a)(b).

3.1.1 From band diagrams to simulation

The band diagrams of different combinations are presented in Fig. 2, in which a positive Conduction Band Offset (CBO) between A1&A2 is defined and shown as Fig. 2 (left), and a negative CBO is as Fig. 2 (right). A positive initial Fermi Level offset (FLO>0) in our model will create a barrier while a negative initial FLO (FLO<0) can provide a driving force after the junction formation, as shown in the figure.

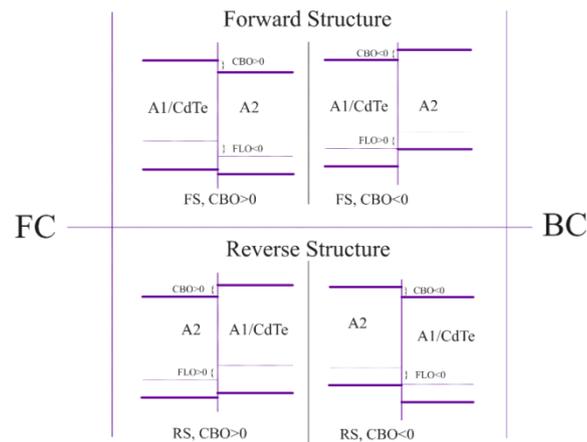


Fig. 2. Band diagrams of different structures before the junction formation. The diagrams are based on bandgap of A2 is 1.4eV. Note that for different structures with a same A2's affinity, the CBO is defined the same in this study.

A comprehensive simulation is firstly performed to test the feasibility of these structures. Herein, only results for 1.5eV&1.4eV are presented, and results about 1.5&1.2eV will also be described if necessary.

3.1.2 Discussions for different structures

The Contour plots of the photovoltaic performances are presented in Fig. 3, where the lateral axis and vertical axis show the CBO and A2's thickness respectively. In Fig. 3, the left column shows simulated results for the reverse structure (labeled as Reverse 100ns, 10ns, and 1ns) while the right column shows results for the forward structure (shown as Forward 100ns, 10ns, and 1ns).

It is easily observed that both structures can have higher efficiency than CdTe-only cells with increased current sometimes (22.5% is the baseline efficiency of CdTe-only cell in our simulation, and the correspondent contour lines are labeled in Fig. 3), and similar results are also obtained for 1.5eV&1.2eV system. These simulation results indicate that a forward structure seems also helpful besides the as-proven reverse structure like FTO/ZMO/CdSe_xTe_{1-x}/CdTe, although it hasn't yet been successfully achieved. Meanwhile, it suggests other materials with lower bandgap values are also potentially applicable for these composite structures if the A1/A2 interface can be buffered through ways like grading similar to CdSe_xTe_{1-x}/CdTe. Additionally, the reverse structure seems to provide somewhat higher results than the forward structure.

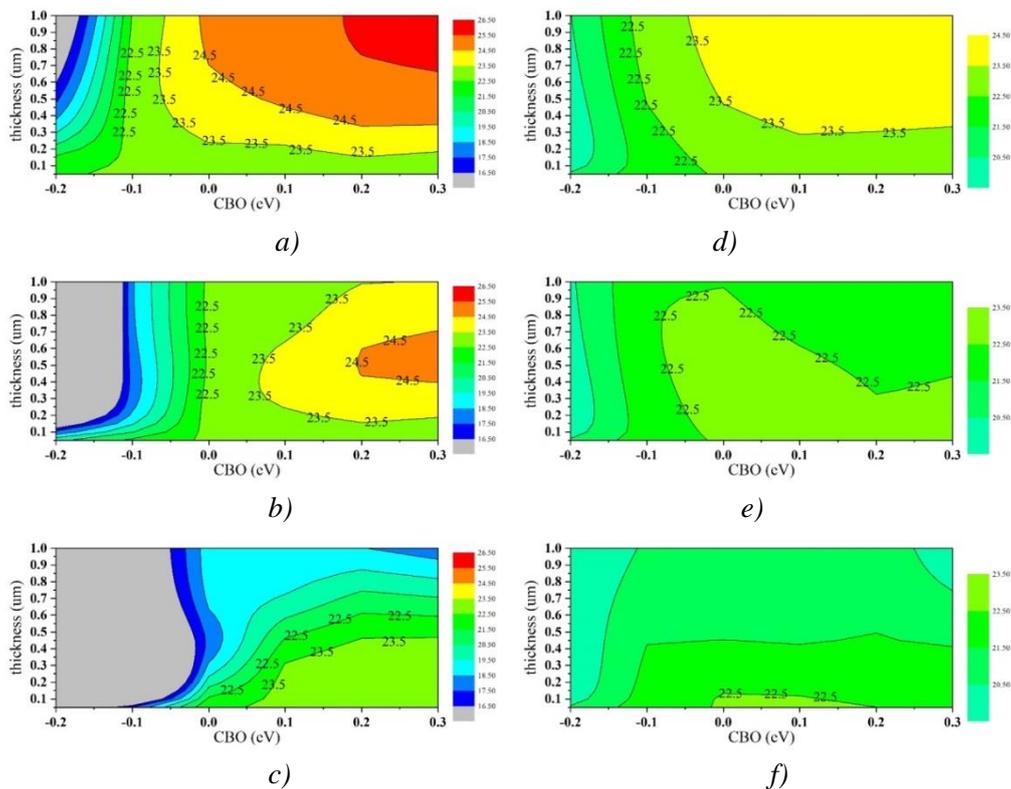


Fig. 3. Contour plots of cell efficiency with varied CdTe/A2 CBO and thickness of A2: (a)Reverse 100ns; (b)Reverse 10ns; (c)Reverse 1ns; (d)Forward 100ns; (e)Forward 10ns; (f)Forward 1ns. 100ns, 10ns and 1ns are the carrier lifetime values of A2. The hole concentrations for both two absorber layers this time are set as $2 \times 10^{14} \text{cm}^{-3}$, comparable to the CdCl₂-treated devices. The thickness of CdTe is 2μm.

It is found that A2 with higher electron affinity (CBO>0) is beneficial for the reverse structure while much lower affinity of A2(CBO<0) for this structure decreases the efficiency by decreasing the current rapidly mostly due to the valence band barrier formed at the interface, preventing hole collection. We found that increasing A2's thickness brings lower current in this case and further simulation shows the more carriers generated in A2, the higher initial bulk recombination and lower QE response. Although there is a driving force at lower A2's affinity, it is merely futile as p-p junction (both are $\sim 10^{14} \text{cm}^{-3}$) in our simulation is not sufficiently powerful. It is thus speculated a higher doping concentration in CdTe promotes transportation in this case and simulation for it proves this speculation. As can be found in the left column, longer A2's carrier lifetime provides higher probability for holes to travel across the valence band barrier before recombination, reducing the initial current losses and extending the feasible beneficial parameter range to smaller affinity or CBO values. With increased CBO, better alignment is formed for better carrier collection, bringing higher efficiency. However, at extremely high A2's affinity, i.e., when CBO is greater than $\sim 0.3 \text{eV}$, obvious FF losses and I-V distortion were observed (not presented) and attributed to the resistance brought by the large positive initial FLO.

The results indicate an appropriately large CBO is beneficial in the reverse structure, however, it doesn't work for the forward structure as much higher A2's affinity would bring a large barrier in the conduction band in this case, preventing electrons generated in A2 transporting to CdTe. We compared this simulation result to actual cases and then speculate that if materials like CdSe_xTe_{1-x} work well when it is inserted between buffer layer and CdTe, it may be not that useful when applied to the back of CdTe unless special treatment. With increasing A2's affinity to much higher values, A2 behaves only like a Back Surface Field (BSF) layer but not an efficient

absorber layer as we found in a QE simulation that the carriers generated in A2 gradually recombine with increased CBO. Longer carrier lifetime and doping concentration of A2 provides higher probability and a driving force for electrons to travel across the conduction band barrier to CdTe before recombination, reducing the J_{sc} decrement and extending the feasible parameter range to higher CBO values. Additionally, even though $CBO < 0$ encourages carrier transportation in a forward structure, bringing it better performances than in the reverse structure with a same CBO, a relatively large positive initial FLO is always detrimental. Based on the results, we regard that the reverse structures usually have better band alignments since a larger-bandgap absorber material can provide better carrier transportation.

In summary, A2 behaves differently in different structures, and in general, a properly large affinity has higher capability to create a higher efficiency for both structures.

3.1.3 Essence for the improved efficiency

The thickness of the absorber influences the recombination and behaves differently for ideal and non-ideal contacts in cells with only one absorber layer. With an ideal contact, recombination increases with the thickness while for non-ideal contacts, things are sometimes the opposite. When there are two absorber layers, the recombination becomes more complicated and there are different mechanisms for the improvement for different structures, dependent of the thickness, as found in our simulation.

Thickness of a generally deposited $CdSe_xTe_{1-x}$ layer in a device is usually around 0.3~1.5 μm . Herein, we extend our simulation to A2's thickness of 2 μm to observe the changes from lower thicknesses to higher ones although the best performances are still within 1 μm . Since $CBO = -0.2eV$ is never good for both reverse and forward structures, it is overlooked this time.

3.1.3.1 For relatively thick absorber (general case)

Curves of *Efficiency vs. Thickness* with various affinities are presented in Fig. 4. In Fig. 4, except for simulated curves of the composite structure, there are two dash lines, representing the baseline efficiency values of CdTe-only cell (2 μm) and A2-only cells with increased A2's thickness, respectively.

In a wide range of material parameters for the cases of 100ns and 10ns, when A2's thickness is less than 400~500nm, the composite structure has a higher efficiency than the CdTe-only or A2-only cells with a same A2's thickness. This characteristic might be helpful for some narrow-gap materials that are difficult to be made thick. With thickness increasing, the efficiency increased to a peak value and then slightly dropped. Worth noting, when A2 is thick enough, we can find in many cases that A2-only cells outperform the composite-one especially when there can be an improvement via adding A2(in Fig. 4(a)(b)(c)(d)). Similar results can be found in simulation for A2's bandgap values between 1.2~1.4eV, but not presented.

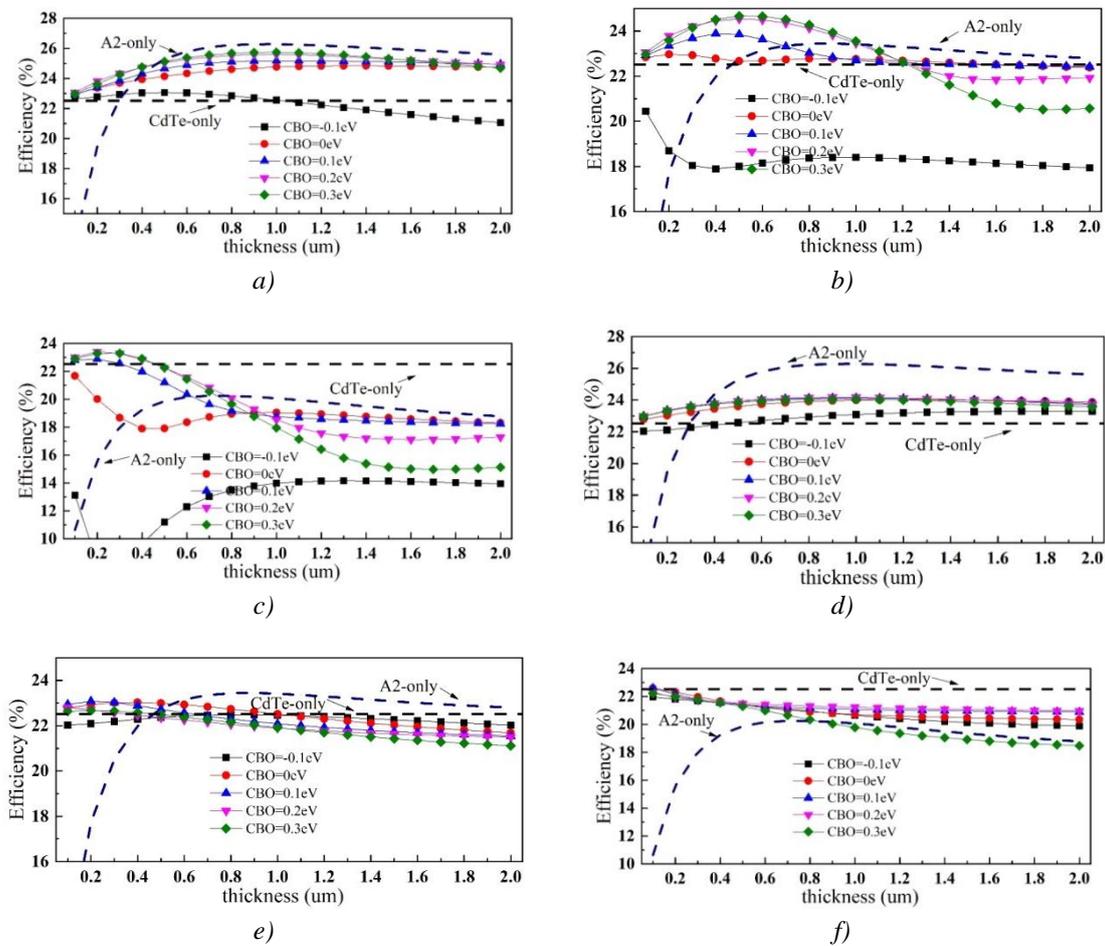


Fig. 4. Curves of Cell efficiency vs. A2's thickness at various A2's affinities. (a)Reverse 100ns; (b)Reverse 10ns; (c)Reverse 1ns; (d)Forward 100ns; (e)Forward 10ns; (f)Forward 1ns. Dash lines of CdTe-only and A2-only cells are plotted for comparison.

This phenomenon is the reason why we extend the thickness range. It indicates that if we had successfully improved the cell efficiency by adding a thick-enough ($> \sim 1 \mu\text{m}$) second absorber layer, we could have simultaneously found that cells with only the second absorber of that thickness always outperforms the composite structure whatever it is a forward or reverse structure. The combination doesn't work better than the higher one. For example, if we see that incorporation of $\text{CdSe}_x\text{Te}_{1-x}$ ($1.1 \sim 1.5 \mu\text{m}$) into CdTe cells helps increase the efficiency dramatically, it is because $\text{CdSe}_{1-x}\text{Te}_x$ ($1.1 \sim 1.5 \mu\text{m}$) itself has the potential to achieve a higher one. For A2 with enough thickness, if CdTe exists in the device, no matter what the position, there is extra recombination besides that in A2. In the reverse structure, CdTe serves as a quasi-neutral region for recombination while in the forward structure, there is larger resistance for carrier transportation especially for carriers generated in CdTe, bringing about extra higher recombination.

According to this, we conclude that the fundamental principle why a second absorber can increase the efficiency apparently by improved the short current is that A2-only cell outperforms the CdTe-only cells and the composite absorber structure as if A2 can be made thick enough. The reason why actual $\text{CdSe}_{1-x}\text{Te}_x$ -only cells are not really good (at least in our lab) might be attributed to the differences between ideal contacts and non-ideal ones. It is also speculated that if A2 is not better than CdTe (like in Fig. 4(c)(f) at large thickness), there won't be any increment by using a composite-absorber structure and cells with only a pure and thick absorber will be the best if the contacts are almost ideal. For real cases, this indicates a combination like CdTe and Si are

not able to achieve efficiency higher than Si solar cell itself. If somebody wants to combined the advantages of the two materials without using tunneling, it's probably futile.

3.1.3.2 For thin layer

Though we applied the principle described above to cases with enough A2's thickness, a discrepancy can be found for lower thickness for the reverse structure in Fig. 4(b)&(c). In these figures, we found peak efficiency values higher than either CdTe-only or A2-only cells notwithstanding the contacts are ideal. The maximum values of different structures and lifetimes values are tabulated in Table 2. These data help to identify the primary cause, namely, the essence and physical mechanisms for the improved efficiency at lower thickness values of A2.

Table 2. Maximum efficiency values for different structures and carrier lifetime values.

case	A2 100ns	A2 10ns	A2 1ns	Reverse 100ns	Reverse 10ns	Reverse 1ns	Forward 100ns	Forward 10ns	Reverse 1ns
Eff (%)	26.28	23.45	20.27	25.74	24.68	23.35	24.18	23.08	22.69

A maximum efficiency of 26.28% in A2-only cell is achieved when carrier lifetime is 100ns, greater than the case of Reverse-100ns and Forward-100ns, correspondent to our conclusions above. However, the reverse structure(10ns&1ns) has a maximum efficiency of 24.68% and 23.35%, respectively, greater than that of A2-only cells (23.45% and 20.27% for 10ns&1ns) or CdTe-only cells (~23%). In fact, there is a wide thickness range between which the composite-structure shows higher efficiency. This phenomenon indicates that a cell with higher efficiency are indeed able to be produced through combination of two different materials with relatively lower efficiency values.

The phenomenon can be also described as the performances of the A2-only cell are improved by adding CdTe at the back. Note that the contacts for all cells are set ideally in our simulation (high-enough work function, low rear surface recombination and high electron barrier), thus we cannot attribute it to the function of CdTe as a reflector since there is no better electron reflector than an optimized ideal back contact.

3.1.3.2.1 Comparison between thin and thick A2

The I-V curves for A2 with different thicknesses (thicknesses=0.7&1.2um are chosen) in A2-only and A2/CdTe structure are plotted in Fig. 5. To further exclude the influence of the current density, CdTe is replaced by a material with a larger bandgap(1.8eV), which has a negligible contribution to the current. The E_v & N_v values for this material are set commensurately with CdTe to keep a same Fermi Level without changing the doping concentration.

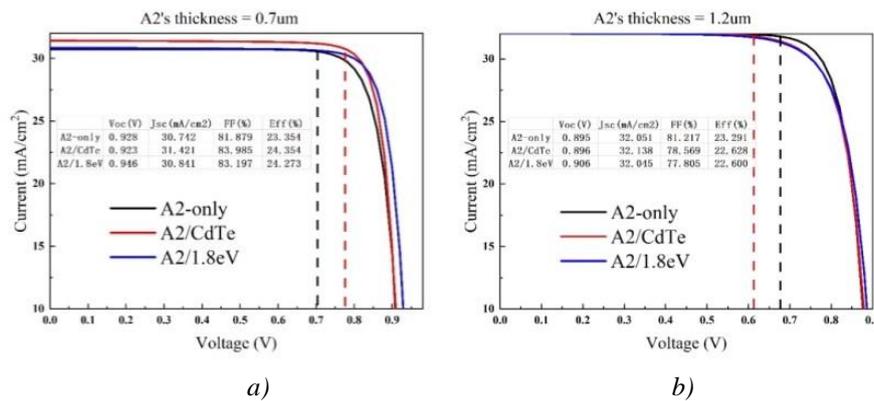


Fig. 5. I-V curves of cells with different structures. (a) A2 is thin (0.7um); (b) A2 is relatively thick (1.2um). CBO=0.2eV. Dash lines in the figures represent critical voltages at which recombination increased dramatically.

For A2 with a thickness of 0.7um, there is an improvement through adding a layer at the back surface whatever the bandgap is 1.5 or 1.8eV. Since the increased current density is less than 1/40 percent of the original one, it is not the only reason. The most important information we can find in Fig. 5(a) is that the applied voltage (defined as a critical voltage, marked by dash lines in Fig. 5) at which the recombination current increased rapidly was improved a little via applying CdTe or other A1. This is the reason why FF increased. However, when A2's thickness increased to 1.2um, adding CdTe brings an efficiency reduction, and we can find the critical voltage was reduced, causing an obvious FF loss. For a same structure, ~5.5% percent loss in FF can be produced if A2's thickness is not controlled carefully. This means CdTe has positive effects on thin A2, but negative effects on thick A2. Meanwhile, A2/1.8eV provides a much higher Voc than A2/CdTe for both thicknesses, indicating that there must be considerable recombination produced by CdTe. Since CdTe or other materials can never be better BSF layer than an ideal back contact, we regard that the function of CdTe or the 1.8eV-A1 is to adjust the electric field distribution at an applied voltage, namely, they alter where the voltage drops. The Voc can be improved to larger than that of with ideal BC, proving that it is not the function of reflecting electrons, but other reasons.

3.1.3.2.2 model description

Some requisites for the observed phenomenon are concluded as:

- (1) In the reverse structure (not found in the forward structure);
- (2) A2 is thin (less than ~1 um);
- (3) CBO is relatively large (0.1~0.3eV); Higher CBO value is detrimental;
- (4) The recombination is majorly limited by A2 and not by CdTe; When A2's carrier lifetime is 100ns, it disappears.

Based on this, herein, we provide a diode model to give a better explanation. The diagrams are presented in Fig. 6.

When there is only A2, the dark current increased exponentially with the applied Voltage (like V_1 in Fig. 6) since the voltage drops nearly completely in FC/A2 junction. For a composite A2/A1 system, when A2 is thin (0.3~0.8um), the depletion region formed in FC/A2 junction sometimes extends into A2/A1 junction, and this means they have interaction. Though the work function of A2 is higher than that of A1 before the junction formation, an initial driving force at A2/A1 interface can still be formed after the junction formation especial when A2 is really thin since carriers in A2 are depleted. With increased applied voltage, the carrier concentration in A2 recovers gradually, forming a small resistance (presented as diode model in Fig. 6). A resistance

like this combining with particular VBO values functions like a back buffer. Though it seems to be detrimental at relatively high voltage, it is speculated that it will not damage the device performances that much since it just emerges at a particular applied voltage in this case. Conversely, this resistance helps to somewhat reduces the voltage drops in FC/A2 junction and this function dominates at this case (i.e., without the barrier, nearly all applied voltage is located in FC/A2 junction). Therefore, the recombination can be somewhat reduced, and the critical voltage is thus increased, as shown in Fig. 5(a). Increasing the thickness of A2 would reduce the interaction between the two junctions gradually, therefore, we observed peak values in Fig. 4(b)(c). When A2 becomes relatively thick, nearly no depletion region of FC/A1 extends to A2/A1 junction whatever the applied voltage, and a complete A2/A1 barrier already exists when there is no applied voltage (shown in Fig. 6). This time, it is harmful and weakens the cell performances, like in Fig. 5(b).

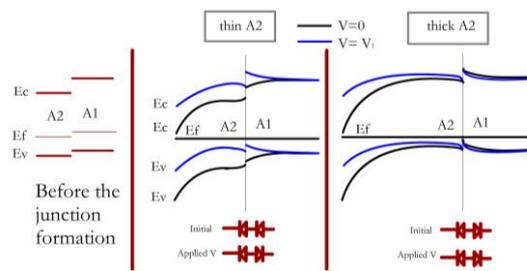


Fig. 6. Diagrams of thin and thick A2 with and without applied V . The front and back contact layers are not depicted in the figure. V_1 is an applied voltage.

There is a little V_{oc} improvement for A2/1.8eV for thickness=1.2 μm , indicating that the two junctions still have some interaction, but the disadvantage is dominant in this case. This V_{oc} increment cannot be reproduced in A2/CdTe or A2/1.4eV (not presented), denoting that the recombination in wide-gap back layer still influences and is required to reduce. Higher A1's bandgap value(>1.8eV) nearly reproduced the same performances for a same A2's thickness (906mV is the maximum V_{oc} value for this carrier density and CBO), and increasing the thickness would eradicate this increment in V_{oc} , substantiating our presumptions. It is easy to find that an extremely large CBO reduces the possibility to create an initial driving force and it is not useful. Since V_{oc} is large for cases with long carrier lifetime of A2, overshadowing the positive effect, so we cannot find peak values in Fig. 4(a).

We examined this model by changing some critical parameters and described as following:

(1) Lowering the electron affinity value of A2(A2: 0.7 μm), i.e., with lower CBO values, the increment disappears, as there is no resistance for altering the voltage drops.

(2) Increasing A2's carrier density to $2 \times 10^{15} \text{cm}^{-3}$ (A2: 0.7 μm), the depletion region is narrowed, and no performance improvement can be observed. Changing A2's carrier density to $2 \times 10^{13} \text{cm}^{-3}$, the improvement still exists and seems a little higher. A little improvement for thickness of 1.2 μm was also observed (not presented).

(3) Changing CdTe's carrier density to $2 \times 10^{15} \text{cm}^{-3}$ (A2: 0.7 μm , CBO=0.2eV), the improvement still exists but is also reduced since the initial barrier height (initial FLO=-0.04eV) is decreased. Higher carrier density to $\sim 10^{16} \text{cm}^{-3}$ eradicates it (initial FLO=-0.02eV, and the depletion region in A1 is narrowed). It is generally regarded a doping at back is beneficial if the lifetime can be controlled simultaneously, but it fails in this case.

The results described above are tabulated in Table 3 and they demonstrate our presumption. (The baseline CBO, doping for A1&A2 are 0.2eV, 2×10^{14} , 2×10^{14} , respectively; The

baseline A2-only cell efficiency values are 23.5%, 23.5%, 24%, 26% for doping ranging from $2E13\sim 2E16\text{cm}^{-3}$).

Table 3. Efficiency of different A1 & A2's parameters.

CBO(eV)	0.2eV	0.1eV	0.3eV						
A2's doping(cm^{-3})	2E14			2E13	2E15	2E16			
A1's doping(cm^{-3})	2E14						2E13	2E15	2E16
Eff(%) for A2/CdTe	24.70	23.48	24.95	25.02	23.57	25.36	24.60	24.11	23.29
Eff(%) for A2/1.8eV	24.28	23.04	24.54	24.61	23.14	25.04	24.25	23.64	22.94

In conclusion, our results indicate that it is still able to combine materials to achieve higher efficiency without deliberate. In our simulation, carrier density of merely $\sim 10^{13}\text{cm}^{-3}$ is able to create a cell efficiency comparable to that of $\sim 10^{15}\text{cm}^{-3}$. This eases the limitation caused by material itself, but the thickness of the material for major absorber layer should be controlled strictly. It can be seen that the benefit of this structure disappears within $\sim 0.5\mu\text{m}$, therefore, we speculate there might be a best thickness value for CdTe. Since we've found that CdTe helps increase the FF, the function of this layer is further discussed in Section 3.2.

3.1.3.3 Extension on cognition for real cells

The relations between Voc and Jsc are considered. It is generally acknowledged that the efficiency of CdTe was improved by the increased current with maintained Voc via introducing selenium. However, our results indicate that we can't simply regard it as the reason.

We've found obvious Voc losses using $\text{CdSe}_{1-x}\text{Te}_x$ as a major absorber even when the carrier lifetime of it is several times of that of CdTe. Particularly, a quick and obvious Voc drop (40~60mV) occurs when the thickness increases from 1 to 2 μm . When CdTe has high-enough carrier lifetime, it is even more difficult to reduce the Voc loss. Combining with the most excellent results provided by First Solar and NREL [23], in which the Voc of CdTe-only cells reaches 921mV while the $\text{CdSe}_x\text{Te}_{1-x}$ /CdTe cells have Voc values between 850~860 mV, we suppose there is actually no so-called maintained Voc.

Similarly, simulations show A2 with even smaller bandgap (1.2~1.3eV) is also able to improve the efficiency by increasing the current, but a more rapid drop in Voc to be comparable to A2-only (1.2~1.3eV) cells occurs within merely tens of nanometers. The commonality between 1.4eV/1.5eV and 1.2~1.3eV/1.5eV systems is not the maintained Voc with increased Jsc. The increased Jsc is requisite but not sufficient, and there must be a trade-off between Voc and Jsc. This trade-off is determined just by the carrier lifetime according to our simulations. For actual cases, this indicates it is not able to maintain the Voc of CdTe by adding Si to absorb long-wave photons, and the Voc will be always comparable to Si-only cells. Thus, we also regard the prevailing statement of "increased current improved the efficiency" is not really accurate. The increased current is merely an apparent performance but not a reason, and it doesn't bring obvious improved efficiency if the carrier lifetime isn't improved. Therefore, we regard only the improved carrier lifetime is the essence for the improvement.

Additionally, our further simulations show (not presented) that adding materials into CdTe cells will never output higher Voc than that of CdTe-only cells with optimal contacts. However, for cases with non-ideal contacts, it's still able to achieve both higher Voc and Jsc via tuning the properties of the front and back layers. This could be somewhat attributed to the selectivity of the actual non-ideal contacts as different contacts are compatible with different material parameters (in terms of electrical properties), and it might be a reason why we sometimes observed a maintained

or even higher V_{oc} when adding $CdSe_xTe_{1-x}$ into $CdTe$ cells. Meanwhile, adding a second absorber sometimes brings much higher improvement for actual non-ideal cases than that of same absorber layers with ideal contacts due to this selectivity according to simulation.

3.2 The Role of the wide-gap absorber layer

3.2.1 Is $CdTe$ really an effective reflector?

Lower bandgap $CdSe_xTe_{1-x}$ shows a positive CBO with $CdTe$ in our model, and some researchers regard that electrons can be reflected by this conduction band barrier. Indeed, $CdTe$ plays a positive role in preventing the electrons being transported to the back surface. However, it is contingent on other parameters and we give some other descriptions. The first question is “is $CdTe$ really an effective electron reflector”, and then, how can we make it effective, namely, in what cases it is effective?

3.2.1.1 influence of the carrier lifetime

We consider the function of $CdTe$ on a general thick-enough A2 layer and performed simulation for CBO between $-0.05\sim 0.25\text{eV}$ ($0.1\pm 0.15\text{eV}$, denoting an initial FLO between $\pm 0.15\text{eV}$) with different A2's carrier lifetime values (1ns, 10ns, 100ns and condition that is controlled by radiative recombination). The results are presented in Fig. 7(a)(b)(c).

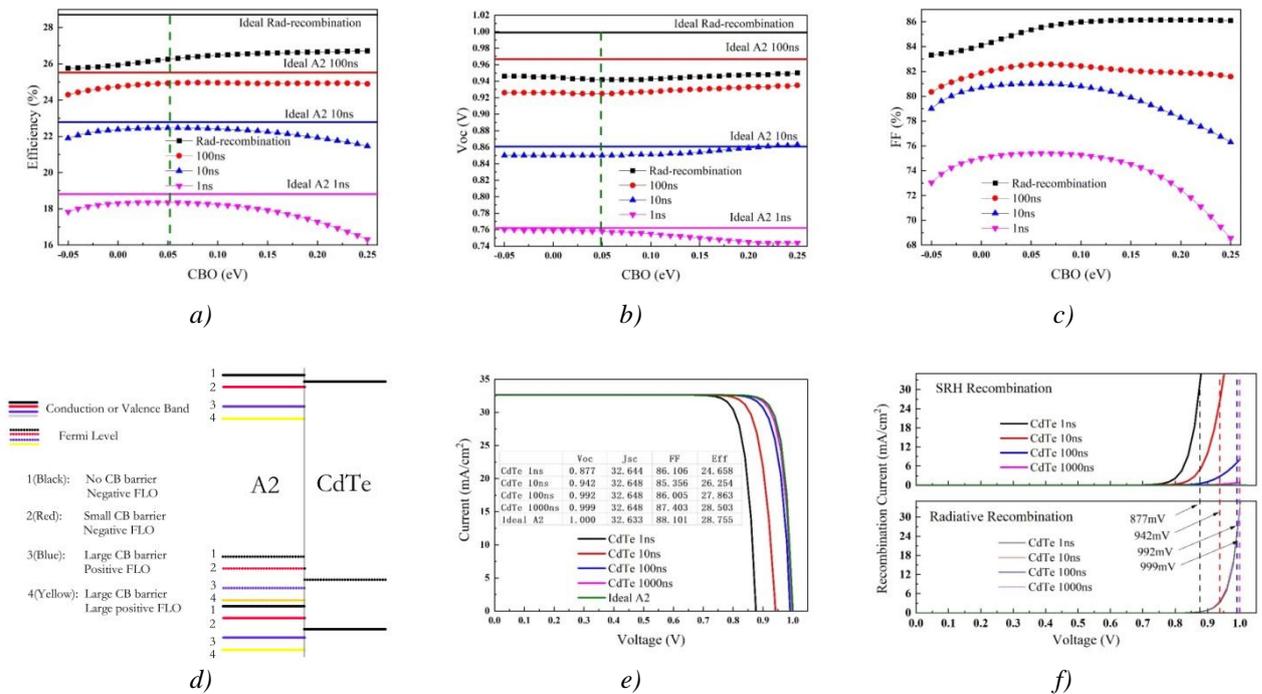


Fig. 7. Cell performances vs. CBO values for different carrier lifetime values. $CdTe$'s thickness is $2\mu\text{m}$. (a)Eff; (b) V_{oc} ; (c)FF; (d)Energy band diagrams for different A2/ $CdTe$ alignments before the junction formation; (e) I-V curves of cells with ideal A2 and different carrier lifetime values of $CdTe$; (f) Recombination for (e).

There are four solid lines with different colors in figures for Eff and V_{oc} (Fig. 7(a)(b)), denoting the ideal performances of these structures. It is found from Fig. 7(b) the V_{oc} exactly increases from a negative CBO to a positive value. This seems to indicate $CdTe$ is an effective reflector when $CBO > 0$, however, it is also observed that efficiency values of all the cases are lower than the case without $CdTe$, i.e., directly contacting with BC. Note that there is no interface recombination considered, proving that there must be some obvious recombination caused by $CdTe$, as mentioned above. We regard there are still some electrons diffusing to $CdTe$ even with $CBO > 0$ since we found an improvement is obtained via changing $CdTe$ to wider bandgap

materials with similar Fermi Level and doping concentration. Additionally, when we change the carrier lifetime of CdTe to lower values (1~5ns), higher losses emerge.

An explanation is given according to the energy band diagram as shown in Fig. 7(d), in which the solid lines represent conduction or valence bands and the dash lines represent correspondent Fermi levels. Four cases of A2/CdTe band alignments are presented with 4 kinds of colors and numbers. The black and red lines (1&2) show the case where there is no or small barrier for electrons to travel from A2 to CdTe accompanied with a negative initial FLO, while the blue and yellow lines (3&4) represent that there is a large barrier and a positive initial FLO. The FLO and CBO interact with each other. When the CBO is less than 0.1eV, there is a negative initial FLO between A2/CdTe, providing a small driving force. However, with decreasing CBO, more electrons can diffuse to CdTe, leading to higher recombination due to the longer travelling distance. When CBO is over 0.1eV, there is a larger barrier for the electrons but a reverse field is formed, and this could bring an FF loss, which is obvious at extremely large CBO values, as shown in Fig. 7(c). Therefore, there might be trade-offs at which recombination is repressed and there's no strong reverse field, bringing highest performances. We can see these trade-offs in Fig. 7 as there are always peaks for the efficiency, corresponding to our speculation. Particularly, when A2 has a very low carrier lifetime, the reverse electric field severely prevents holes being collected by the back contact, bringing about more recombination in A2 and an obvious Voc loss, unlike the Voc increase for higher carrier lifetime.

It is observed from Fig. 7(a) that even there are small barriers accompanied with little driving force, for the cases limited by radiation recombination, CdTe with carrier lifetime of 10ns is not enough to support a high Voc. Therefore, the cell efficiency with different CdTe lifetimes is again investigated and presented in Fig. 7(e)(f). The radiation-limited cells have an efficiency of 28.7% and a Voc of 1V in our model (a little less than the precise S-Q limit). Herein, we examined the case with CBO=0.05eV (other cases are similar). It is found that CdTe limits the cell efficiency especially on the Voc by increasing the SRH recombination (shown in Fig. 7(f)). The Voc values obtained in these devices are close to that of CdTe-only cells, suggesting that CdTe is the dominant influencing factor. Even the Voc of 1V for ideal-A2 device can be obtained with ideal contacts, it is not possible to fully realize it with carrier lifetime of CdTe is only 1~10 ns. For CdTe, more excellent A2 won't limit, however, (2+2um)-A2/CdTe is no better than pure 4um-A2. Only when Voc limited by CdTe is much larger than that by A2, there won't be obvious decrement. All these simulations indicate CdTe is not an effective reflector unless modified, and for an actual device, to harness CdSe_xTe_{1-x} as the major absorber layer and improve its carrier lifetime for better performances in the future, it is required to simultaneously improve the carrier lifetime of CdTe. In this way, CdTe can be applied as an effective reflector.

3.2.1.2 function of doping

Achieving high carrier lifetime for CdTe is difficult and for state-of-art technology is not significant since the device is still majorly limited by CdSe_xTe_{1-x} and improving CdTe lifetime just brings negligible escalation according to extra simulations. To balance between the CBO and the initial FLO, adulteration seems to be helpful, and a hole density of 10^{16-17}cm^{-3} without damaging the carrier lifetime is now achievable [24~27].

Cell efficiency values with different CdTe doping concentrations are plotted in Fig. 8. The dash line denotes the cell efficiency with ideal contacts. From Fig. 8, it can be seen that higher doping concentration effectively reduces the losses caused by CdTe. For small even negative CBO (-0.05eV and 0.05eV), it shows that 10^{15}cm^{-3} is nearly enough to maintain the efficiency near to the ideal contact. Cell efficiency is not sensitive to the thickness with carrier concentration over 10^{15}cm^{-3} in these cases. However, with increased CBO, in order to create a negative initial FLO, higher carrier concentration is required, and we saw larger differences at CBO between 0.15~0.25eV. In this range, cell efficiency is more susceptible to carrier concentration.

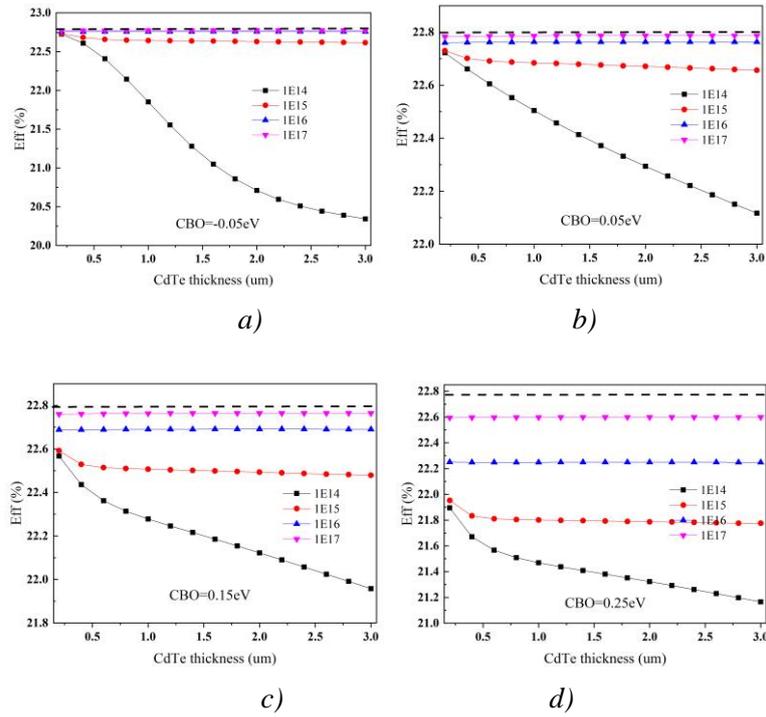


Fig. 8. Cell Efficiency with different doping concentrations of CdTe for different CBO values. The thickness is from 0.2~3um. Carrier lifetime of A2 is 10ns. The doping concentration of CdTe ranges from 10^{14} to 10^{17}cm^{-3} . (a) CBO=-0.05eV; (b) CBO=0.05eV; (c) CBO=0.15eV; (d) CBO=0.25eV.

It suggests generally a doping of 10^{16}cm^{-3} is required and enough to be an effective reflector, while $\sim 10^{14} \text{cm}^{-3}$ is never sufficient (when carrier lifetime of A2 is larger, it becomes more obvious). Nevertheless, for extremely large CBO, to realize a negative initial FLO, much higher doping is required. An efficiency loss between 1~2 percent is caused if CdTe is thick and without deliberate adulteration. On the other hand, higher doping provides higher ability for CdTe to achieve higher Voc, decreasing the bulk recombination in CdTe. Both improved driving force and decreased SRH recombination are the reasons for the improved efficiency. We further perform simulations on different bandgaps of A1 with same conduction band energy and same Fermi Level, but varied carrier concentration (For example, CdTe: $4.3+1.5eV$, doping 2E16, A1: $4.3+1.56eV$, doping 2E15), the results are nearly the same, indicating a good band alignment no matter what the doping is appropriate, notwithstanding different doping would show distinctive compatibility with the BC layer in actual cases. Further simulations also demonstrate that A1 with lower affinity but a same Fermi Level produces results commensurate with the case with CdTe as the minor absorber.

Based on the simulation above, we conclude CdTe without enough doping is not an effective reflector for any kind of A2/CdTe CBO when the contact is ideal. The cell performances are still influenced a lot by CdTe especially for the cases with high carrier lifetime of the major absorber(A2) or low carrier lifetime of CdTe. It can be speculated here that thinner CdTe as the minor absorber would be better, but this is solely the essence for the cases with ideal contacts, and non-ideal contacts may bring different results.

3.2.2 A1 as a back highly-resistant layer

Section 3.1.3.2 shows a higher efficiency was achieved by combining two materials, and we regard the role of A1 in this case is as a back highly-resistant layer. Herein, we test the thickness, doping concentration for an individual A2. Since we find that CdTe with 10ns is not able to fully repress the bulk recombination (Fig. 5(b)), here, we change (E_g+E_c) values from

(1.5+4.3) to (2.5+3.3) to inhibit recombination brought by A1 while maintaining the same E_v and Fermi Level values. In this section, we are going to show how a wide-gap layer functions as a back highly-resistant layer for thin absorber to render cell performances better than the cases with ideal contacts and applied the rules to real cases. Although the photons are not completely collected, it still contributes to higher efficiency.

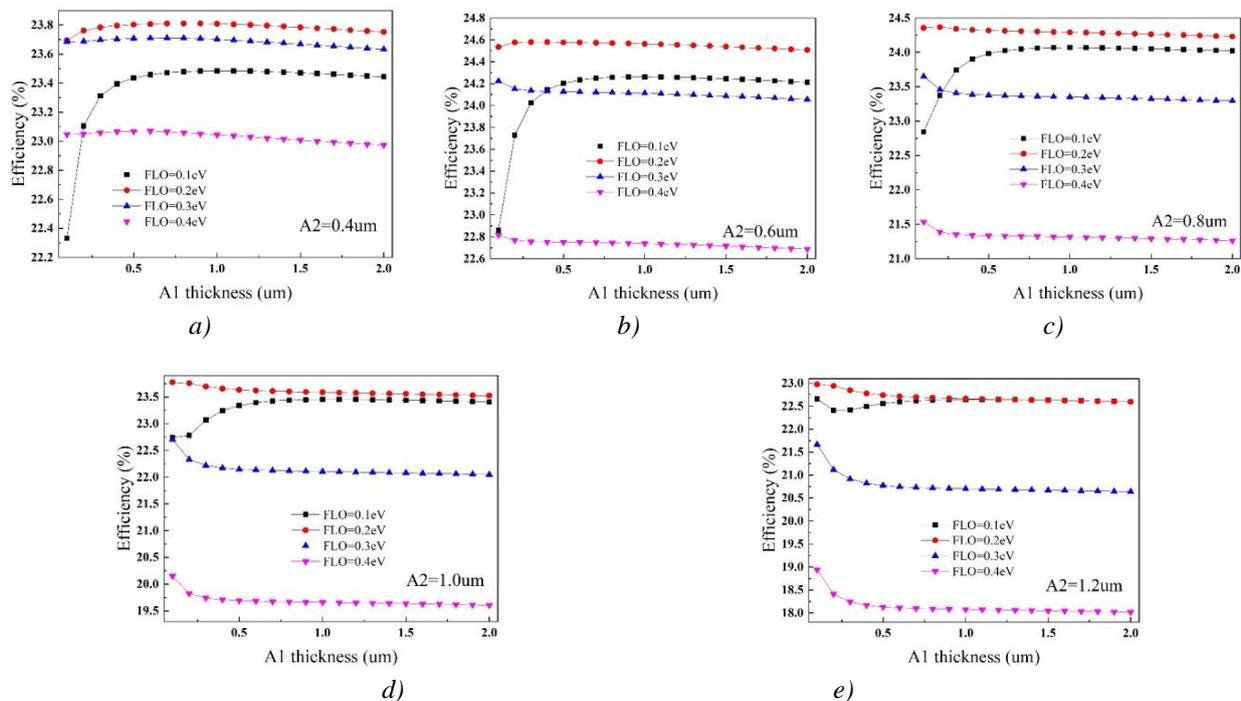


Fig. 9. Cell Efficiency with different A1's thicknesses for thin A2. (a)~(e): A2=0.4, 0.6, 0.8, 1.0, 1.2um. The carrier lifetime and density are 10ns and $2 \times 10^{14} \text{cm}^{-3}$ for both A1&A2. FLO refers to the initial Fermi Level offset before the junction formation.

Unlike demonstrated in Fig. 8 that the efficiency always decreases with A1's thickness whatever the CBO values. For thin A2, sometimes it increases, as shown in Fig. 9. The efficiency for A1-only cells at various thicknesses are (22.0%, 23.1%, 23.4%, 23.4%, 23.3%) for 0.4~1.2um, and 23.4% is nearly the maximum efficiency for A2-only cells with ideal contacts in this model. It is observed an obvious improvement is possible for FLO between 0.1~0.3eV when A2's thickness is less than 800nm. The highest efficiency is 24.6%. When FLO is beyond 0.3eV, it declines as a large FF loss occurs even though V_{oc} is improved. With increased A1's thickness, there is a peak value, indicating that several hundred nanometers are required to realize a positive interaction. Higher FLO decreases the probability to realize an initial driving force according to the mechanisms described in 3.1.3.2.2, thus it reaches the maximum at low thickness, and an extremely large FLO brings a failure quickly, thus no improvement is observed. Worth mentioning, though CdTe brings some recombination, by using it as the back layer, it brings efficiency greater than 25% as it contributes to the current if the thickness is controlled carefully. In this sense, we are able to successfully using material with efficiency of 23% to reach 25% without high carrier lifetime and doping. Therefore, a relatively large thickness for CdTe as A1 is beneficial. A rough estimation shows that 500~1000 nm is appropriate for the maximum efficiency.

What's significant to mention in our simulation is that our findings are merely suitable for A2's bandgap values smaller than 1.4eV. Higher energy bandgap may bring losses especially

when there isn't ideal contact because a large-gap material can create higher Voc, and at this time, recombination increased a lot at higher applied voltage, overshadowing the positive function of the barrier. In our opinion, one way to realize a high efficiency is to use a thin lower-bandgap material with a wider-bandgap one as a back highly-resistant layer. Although this method is not very helpful to realize an efficiency comparable to the ideal states, it could reduce the cost and ease the manufacture since the requirement for material quality and doping can be lowered a lot.

4. Conclusions

In this paper, the working mechanisms for solar cells with a CdTe-based composite-absorber layer are thoroughly investigated. Our results show materials with a lower gap between 1.2~1.4eV have capacity to improve the efficiency of CdTe cells at particular circumstances whatever they are inserted between the front or rear contact and CdTe. The materials put in front of CdTe perform better than at the back of it for the better band alignments in most cases. We explored the essence of the improved cell performances in different occasions. For most cases with thick A2, the improvement brought by adding A2 is attributed to that A2-only cells outperform the composite structure.

For particular thin-A2 cases, we found a thin major absorber combined with a highly-resistant wide-gap layer has potential to perform better than a pure one and provided diode model to explain it. This may be useful for lowering the cost and easing the manufacturing. Additionally, we demonstrated that there is no so-called maintained voltage with increased current in essence even at a relatively high A2's carrier time, especially when CdTe itself can achieve a high voltage and A2 is thick. We regard current increment is just an apparent performance, and the only reason for the improved efficiency is the carrier lifetime, which determines the trade-off between voltage and current. Besides, we proved that CdTe is not an effective reflector without high-enough doping even with optimal contacts especially for large A2/CdTe CBO values and long A2's carrier lifetime in essence, thus higher carrier lifetime of CdTe is also required for further development.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 6170 4115). The authors acknowledge the use of SCAPS software developed and supported by Dr. Marc Burgelman and colleagues at the University of Gent in all the simulations reported in this paper.

References

- [1] A. H. Munshi, J. M. Kephart, A. Abbas, T. M. Shimpi, K. L. Barth, J. M. Walls, W. S. Sampath, *Solar Energy Materials and Solar Cells* **176**, 9 (2018).
- [2] A. Wang, T. Tang, S. Ren, J. Zhang, L. Wu, W. Li, W. Wang, L. Feng, *Materials Science in Semiconductor Processing* **94**, 28 (2019).
- [3] D.-B. Li, Z. Song, R. A. Awni, S. S. Bista, N. Shrestha, C. R. Grice, L. Chen, G. K. Liyanage, M. A. Razooqi, A. B. Phillips, M. J. Heben, R. J. Ellingson, Y. Yan, *ACS Applied Energy Materials* **2**(4), 2896 (2019).
- [4] M. Lingg, A. Spescha, S. G. Haass, R. Carron, S. Buecheler, A. N. Tiwari, *Sci Technol Adv Mater* **19**(1), 683 (2018).

- [5] D. E. Swanson, J. R. Sites, W. S. Sampath, *Solar Energy Materials and Solar Cells* **159**, 389 (2017).
- [6] T. Ablekim, J. N. Duenow, X. Zheng, H. Moutinho, J. Moseley, C. L. Perkins, S. W. Johnston, P. O'Keefe, E. Colegrove, D. S. Albin, M. O. Reese, W. K. Metzger, *ACS Energy Letters* **5**, 892 (2020).
- [7] A. H. Munshi, J. Kephart, A. Abbas, J. Raguse, J.-N. Beaudry, K. Barth, J. Sites, J. Walls, W. Sampath, *IEEE Journal of Photovoltaics* **8**(1), 310 (2018).
- [8] B. Lv, B. Yan, Y. Li, C. Sui, *Solar Energy* **118**, 350 (2015).
- [9] C. Li, J. Poplawsky, N. Paudel, T. J. Pennycook, S. J. Haigh, M. M. Al-Jassim, Y. Yan, S. J. Pennycook, *IEEE Journal of Photovoltaics* **4**(6), 1636 (2014).
- [10] D. W. Lane, *Solar Energy Materials and Solar Cells* **90**(9), 1169 (2006).
- [11] T. A. M. Fiducia, B. G. Mendis, K. Li, C. R. M. Grovenor, A. H. Munshi, K. Barth, W. S. Sampath, L. D. Wright, A. Abbas, J. W. Bowers, J. M. Walls, *Nature Energy* **4**(6), 504 (2019).
- [12] X. Zheng, D. Kuciauskas, J. Moseley, E. Colegrove, D. S. Albin, H. Moutinho, J. N. Duenow, T. Ablekim, S. P. Harvey, A. Ferguson, W. K. Metzger, *APL Materials* **7**(7), 071112 (2019).
- [13] C. Li, A. Wang, L. Wu, X. He, J. Zhang, X. Hao, L. Feng, *Materials Research Express* **6**(6), 066415 (2019).
- [14] T. Baines, G. Zoppi, L. Bowen, T. P. Shalvey, S. Mariotti, K. Durose, J. D. Major, *Solar Energy Materials and Solar Cells* **180**, 196 (2018).
- [15] J. M. Kephart, J. W. McCamy, Z. Ma, A. Ganjoo, F. M. Alamgir, W. S. Sampath, *Solar Energy Materials and Solar Cells* **157**, 266 (2016).
- [16] G. Sozzi, F. Troni, R. Menozzi, *Solar Energy Materials and Solar Cells* **121**, 126 (2014).
- [17] T. Song, A. Kanevce, J. R. Sites, *Journal of Applied Physics* **119**(23), 233104 (2016).
- [18] Y. Li, J. Li, X. Yin, Q. Chen, W. Wang, L. Wu, X. Hao, J. Dong, *Chalcogenide Letters* **16**(11), 535 (2019).
- [19] M. Mostefaoui, H. Mazari, S. Khelifi, A. Bouraiou, R. Dabou, *Energy Procedia* **74**, 736 (2015).
- [20] J. Sites, J. Pan, *Thin Solid Films* **515**(15), 6099 (2007).
- [21] J. N. Duenow, W. K. Metzger, *Journal of Applied Physics* **125**(5), 053101 (2019).
- [22] J. Moseley, W. K. Metzger, H. R. Moutinho, N. Paudel, H. L. Guthrey, Y. Yan, R. K. Ahrenkiel, M. M. Al-Jassim, *Journal of Applied Physics* **118**(2), 025702 (2015).
- [23] W. K. Metzger, S. Grover, D. Lu, E. Colegrove, J. Moseley, C. L. Perkins, X. Li, R. Mallick, W. Zhang, R. Malik, J. Kephart, C. S. Jiang, D. Kuciauskas, D. S. Albin, M. M. Al-Jassim, G. Xiong, M. Gloeckler, *Nature Energy* **4**(10), 837 (2019).
- [24] J. J. McCoy, S. K. Swain, J. R. Sieber, D. R. Diercks, B. P. Gorman, K. G. Lynn, *Journal of Applied Physics* **123**(16), 161579 (2018).
- [25] B. E. McCandless, W. A. Buchanan, C. P. Thompson, G. Sriramagiri, R. J. Lovelett, J. Duenow, D. Albin, S. Jensen, E. Colegrove, J. Moseley, H. Moutinho, S. Harvey, M. Al-Jassim, W. K. Metzger, *Sci Rep* **8**(1), 14519 (2018).
- [26] B. McCandless, W. Buchanan, G. Sriramagiri, C. Thompson, J. Duenow, D. Albin, S. A. Jensen, J. Moseley, M. Al-Jassim, W. K. Metzger, *IEEE Journal of Photovoltaics* **9**(3), 912 (2019).
- [27] A. Nagaoka, D. Kuciauskas, J. McCoy, M. A. Scarpulla, *Applied Physics Letters* **112**(19), 192101 (2018).