

Can we improve the record efficiency of CdS/CdTe solar cells?

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Available online 18 April 2006

Abstract

Polycrystalline thin film CdTe continues to be a leading material for the development of cost effective and reliable photovoltaic systems. The two key properties of this material are its near ideal band gap for photovoltaic conversion efficiency of 1.45 eV, and its high optical absorption coefficient. Thin film CdTe solar cells are typically hetero-junctions with CdS being the n-type partner, or window layer. Efficiencies as high as 16.5% have been achieved.

In this paper we make a physical analysis of the typical CdS/CdTe superstrate solar cell, and we show that present record efficiencies are very close to the practical efficiency limit for a CdS/CdTe hetero-junction cell. We show that a current estimate for the maximum efficiency of hetero-junction CdS/CdTe solar cells is around 17.5%, in contrast to old theoretical predictions, which calculate about 30% efficiencies for ideal homo-junction CdTe solar cells. This analysis explains why the record efficiency for this kind of cells has been stable for the last 10 years, going up by less than 1% from 15.8% to only 16.5%.

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Keywords: Thin film solar cells; CdTe; CdS

1. State of the art for CdS/CdTe solar cells

The typical superstrate structure of a CdTe/CdS solar cell is composed of 4 layers: a transparent and conducting oxide (TCO) which acts as a front contact, a CdS film which is the so-called window layer, a CdTe film which is the absorber layer made on top of CdS and the back contact on top of the CdTe layer.

The characteristics that are required in order for a TCO to be used as a front contact for CdTe/CdS thin film solar cells are: high transparency, better than 85% in the wavelength

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region of interest (400–860 nm); low resistivity on the order of $2 \times 10^{-4} \Omega \text{ cm}$ or a sheet resistance less than $10 \Omega/\text{square}$; good stability at the maximum temperature at which other layers are prepared. This means that no diffusion from the TCO into the layers deposited subsequently must happen. In Table 1 the properties of some of the most important materials used as TCO in solar cells [1] are shown. Of particular interest is Cd_2SnO_4 which has a transparency above 85% and resistivity as low as $2 \times 10^{-4} \Omega \text{ cm}$.

It is possible to take advantage of the different properties of two TCOs by forming a bi-layer. High-efficiency CIGS and CdTe devices are generally fabricated with such bi-layer structures, consisting of a highly conducting layer for low-resistance due to contact and lateral current collection and a much thinner high-resistivity layer (called buffer layer) of a suitable material, to minimize forward current through pinholes in the window layer. By incorporating a 50 nm thick resistive SnO_2 , In_2O_3 , ZnO , or Zn_2SnO_4 layer, the CdS layer thickness can be reduced to $< 80 \text{ nm}$, which significantly improves the blue response of the CdTe devices. The presence of the smoother high-resistive layer also improves the CdS film morphology by providing large grains during chemical bath deposition (CBD).

CdS is prepared by several methods that are evaporation, CBD and closed-space sublimation (CSS). All these methods are suitable to prepare a CdS layer that, when used in CdTe/CdS solar cells, can give efficiencies larger than 10% even though the highest efficiency was obtained by using a CdS prepared by CBD. The choice of the CBD method was probably due to the fact that CBD makes a very compact film that covers perfectly the TCO layer.

A very important treatment independent of the deposition technique for both CdS and CdTe layers is a thermal annealing after deposition of CdCl_2 on top of the CdTe layer. If the CdCl_2 treatment is not performed, the short circuit current and the efficiency of the solar cell are very low. The treatment consists in depositing 300–400 nm of CdCl_2 on top of CdTe with a subsequent annealing at 400°C for 15–20 min in air or in an inert gas like Ar. During this process the small CdTe grains are put in vapour phase and re-crystallize giving a better-organized CdTe matrix. The presence of Cl_2 could favour the crystalline growth of CdTe by means of a local vapour phase transport. In this way the small grains disappear, and the CdS/CdTe interface is reorganized.

Owing to its optoelectronic and chemical properties, CdTe is an ideal absorber material for high-efficiency low-cost thin film polycrystalline solar cells. CdTe is a direct band gap material with an energy gap of 1.5 eV, and an absorption coefficient $\sim 10^4 \text{ cm}^{-1}$ in the visible region, which means that a layer thickness of a few micrometers is sufficient to

Table 1

Properties of some of the most common transparent conducting oxides (TCO) and buffer layers.

Material	Resistivity ($\Omega \text{ cm}$)	Transparency (%)
SnO_2	8×10^{-4}	80
$\text{In}_2\text{O}_3:\text{Sn}$ (ITO)	2×10^{-4}	> 80
$\text{In}_2\text{O}_3:\text{Ga}$ (IGO)	2×10^{-4}	85
$\text{In}_2\text{O}_3:\text{F}$	10^{-2}	85
Cd_2SnO_4 (CTO)	2×10^{-4}	85
Zn_2SnO_4 (ZnTO)	10^{-2}	90
$\text{ZnO}:\text{In}$	8×10^{-4}	85

absorb 90% of the incident photons. Owing to the high deposition temperature in most cases, the films are deposited with Cd deficiency, giving rise to p-type conductivity. Because of the high ionicity (72%) of CdTe, the crystallites formed are well-passivated and strong chemical bonding (5.75 eV) results in high chemical and thermal stability. CdTe solar cell devices have proven to be remarkably tolerant to the deposition method and devices with efficiency >10% have been fabricated by several deposition techniques. Some of these techniques, CSS, electro-deposition and screen-printing have been scaled to yield large area modules. Solar cells based on CdS/CdTe junction have achieved an efficiency of 16.5% in small areas compared with the theoretical maximum efficiency of 29% for homo-junction CdTe cells. For the past 10 years the record efficiency has changed from 15.8% to 16.5% only.

There are no low-cost metals available with appropriate high work function (>4.5 eV) to form ohmic contact on CdTe and Au has been used in most cases. Ni-based contacts have also shown promising results. In an alternative approach a pseudo-ohmic contact was developed for CdTe devices. Here, a highly doped semiconductor is first deposited/formed on the CdTe surface followed by the application of a metal film contact. Semiconductors such as HgTe, ZnTe:Cu, Cu_xTe, and Te can be deposited between CdTe and the contact metal to achieve a good ohmic contact. Cu-doped graphite paste and antimony telluride have also been tried, with mixed success. Etching of CdTe films using Br–methanol, NP solution, etc., creates a Te-rich p⁺ region, which can be useful in making a pseudo-ohmic contact with Cu/Au layer, since the use of elemental Cu leads to p²⁺ Cu₂Te formation. Wet contacting methods and all-vapour contacting methods are actively being investigated for commercial development.

All of the above ideas have been developed in order to obtain high efficiency CdS/CdTe solar cells. The team lead by X. Wu in the NREL in USA has achieved the highest efficiency for this kind of solar cells [2]. In Fig. 1 we show the structure and approximate thickness for each layer with which they have attained conversion efficiency of 16.5%. Notice the presence of the mentioned CTO and ZnTO bilayer for the TCO. Notice also

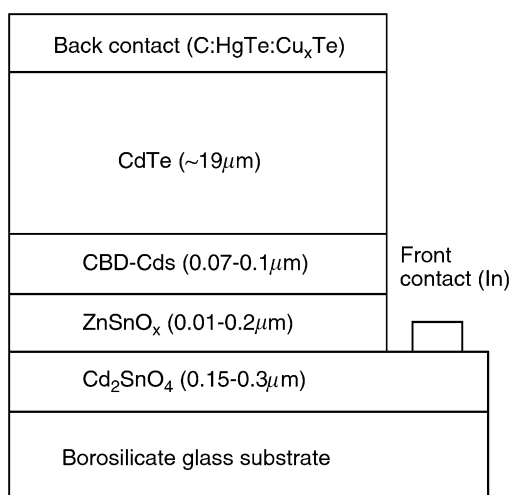


Fig. 1. CTO/ZTO/CdS/CdTe record efficiency solar cell device structure.

that they have used a 10 μm CdTe layer, but with a very thin CdS layer below 0.1 μm. The graphite contact at the back of the CdTe layer usually contains Cu as seems to be needed in order to make good ohmic contacts on p-type CdTe. For their highest efficiency solar cell: $V_{oc} = 845\text{ mV}$, $J_{sc} = 25.88\text{ mA/cm}^2$, $FF = 75.5\%$, $\eta = 16.5\%$.

2. Can we improve the efficiency of CdS/CdTe solar cells?

In order to answer the above question some data on the properties of CdS and CdTe films is needed. We must notice that the diverse preparation techniques for CdS and CdTe layers cause also variation in material properties such as carrier lifetime and mobility and absorption coefficient. Unfortunately, much of the work is done empirically and no design or optimization methodology is followed since these characteristics should be known but usually they are not when making solar cells.

In Table 2, we show some of the properties of CdS as has been reported by people doing simulation of CdS/CdTe solar cells. As we shall see, these values allow us to draw the ideal band-diagram at the hetero-junction with CdTe in a solar cell. The donor concentration will depend strongly on the deposition method, but a desirable value of 10^{17} cm^{-3} is given here. If this value could be increased to $1 \times 10^{18}\text{ cm}^{-3}$ by some doping process we could expect better results for the solar cell open circuit voltage.

In Table 3, similar properties for CdTe thin films are shown. Notice that with these values the electron diffusion length would be approximately 8 μm. However, due to the diverse quality of the CdTe deposited in different laboratories with different deposition techniques we can expect values between 1 and 8 μm. The majority carrier concentration is also very low, about $1 \times 10^{15}\text{ cm}^{-3}$. Increasing this value to 10^{16} cm^{-3} should also help to increase the built-in voltage of a CdS/CdTe solar cell.

From the preceding data, we can now draw the ideal band diagram for the CdS/CdTe hetero-junction as shown in Fig. 2. A built-in voltage of 0.95 V is expected. The conduction band discontinuity does not limit the electron photocurrent from CdTe to CdS. The hole photo-current from CdS to CdTe is not limited either by the valence band discontinuity.

As explained before, we have found a variety of data for the absorption coefficient of CdTe. This property and how it varies as a function of wavelength is a very important parameter and determines the CdTe layer thickness required for absorbing the sunlight radiation. The data used in our calculations corresponds to values reported for crystalline CdTe [3].

In order to establish an approximate estimation of the appropriate CdTe thickness, in Fig. 3 we show the relative cumulative carrier generation rate, i.e., the total amount of

Table 2
Typical electrical parameters for CdS films, according to different published reports

Parameter	Value	Parameter	Value
ϵ_s	9.0	N_A	0.0
μ_n	$350\text{ cm}^2/\text{V s}$	N_D	$1 \times 10^{17}\text{ cm}^{-3}$
μ_p	$50\text{ cm}^2/\text{V s}$	E_g	2.42 eV
N_C	$1.8 \times 10^{19}\text{ cm}^{-3}$	χ	4.5 eV
N_V	$2.4 \times 10^{18}\text{ cm}^{-3}$	Thickness	0.1 μm
τ	$2 \times 10^{-10}\text{ s}$		

Table 3
Similar typical electrical parameters for CdTe films

Parameter	Value	Parameter	Value
ϵ_s	9.4	N_A	$1 \times 10^{15} \text{ cm}^{-3}$
μ_n	$500 \text{ cm}^2/\text{Vs}$	N_D	0.0
μ_p	$60 \text{ cm}^2/\text{Vs}$	E_g	1.5 eV
N_C	$7.5 \times 10^{17} \text{ cm}^{-3}$	χ	4.28 eV
N_V	$1.8 \times 10^{18} \text{ cm}^{-3}$	Thickness	1–10 μm
τ	$1.6 \times 10^{-8} \text{ s}$		

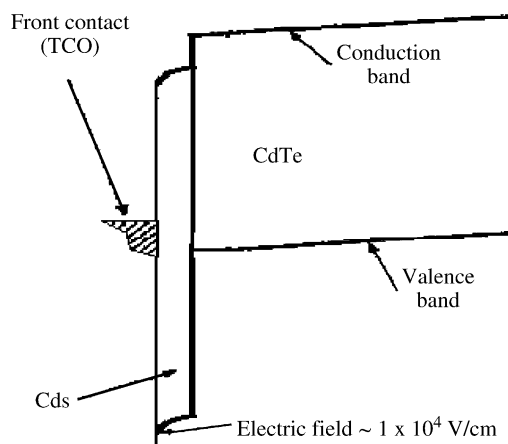


Fig. 2. Ideal band diagram at the CdS/CdTe interface. $\Delta E_C = 0.22 \text{ eV}$ and $\Delta E_V = 0.7 \text{ eV}$. The total built-in voltage is around 0.95 V when the doping at each side of the hetero-junction is assumed to be $N_D = 1 \times 10^{17} \text{ cm}^{-3}$ and $N_A = 1 \times 10^{15} \text{ cm}^{-3}$, respectively.

carriers generated per unit area in the CdTe volume taking into account the absorbed solar spectrum photons from the surface up to position x inside this layer. The spectrum taken was the AM1.5 global normalized to 100 mW/cm^2 . The graph shows the cumulative generation rate normalized to the total photon content in this spectrum. For CdTe thickness sufficiently large, the total generated carriers will be approximately 100% of what can be obtained from the solar spectrum assuming that one electron–hole pair is generated for each photon absorbed.

This graph indicates that an estimated optimum value for the CdTe thickness is between 2 and $4 \mu\text{m}$, since little gain is expected for the photo-current if the thickness is increased above $4 \mu\text{m}$, and degradation of the series resistance may cause a reduction of the filling factor. Below $2 \mu\text{m}$ the photo-current would degrade quickly as the thickness becomes smaller.

In order to be more precise, a detailed calculation has to be made, taking into account the carrier losses by recombination in this layer. This calculation can be made assuming the CdTe layer as a uniform semiconductor by solving the carrier transport equations in this region. For x measured from the CdTe edge at the interface, the collection probability for

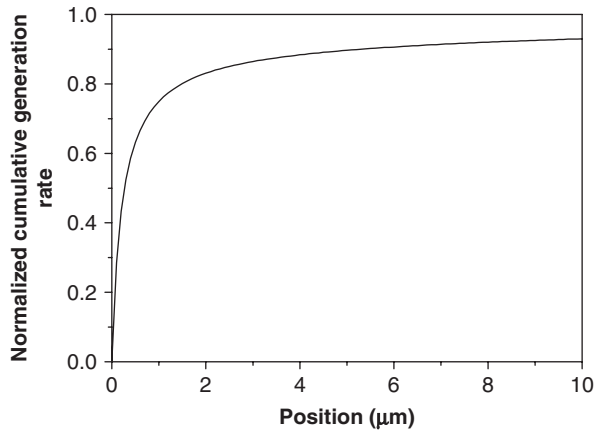


Fig. 3. Normalized cumulative generation rate (total number of electron–hole pairs generated per unit area per unit time) as a function of position in the volume of the CdTe film. The global solar spectrum AM1.5 was assumed (normalized to 100 mW/cm²).

electrons generated at position x can be calculated as

$$P_c(x) = \left\{ \begin{array}{l} 1 \rightarrow x \leq W_{scr} \\ \frac{\cosh\left(\frac{W_b - x}{L_n}\right) + \frac{SL_n}{D_n} \sinh\left(\frac{W_b - x}{L_n}\right)}{\cosh\left(\frac{W_b - W_{scr}}{L_n}\right) + \frac{SL_n}{D_n} \sinh\left(\frac{W_b - W_{scr}}{L_n}\right)} \rightarrow W_{scr} < x < W_b \end{array} \right\}, \quad (1)$$

where W_b is the CdTe layer thickness, W_{scr} is the space charge region length within the CdTe layer, L_n and D_n are the diffusion length and diffusion coefficient for electrons, respectively, and S is the recombination velocity at the back contact.

Hence, the electron current density can be calculated by

$$J_e = q \int_{AM1.5} d\lambda N_O(\lambda) \int_0^{W_b} [P_c(x) \alpha(\lambda) \exp(-\alpha(\lambda)x)] dx, \quad (2)$$

where q is the electron charge magnitude, $\alpha(\lambda)$ is the absorption coefficient for photons with wavelength λ and N_O is the number of incident photons per unit area per unit time in the wavelength range between λ and $\lambda + d\lambda$ at the CdTe surface. Notice that the integral with respect to x corresponds to the cell's internal quantum efficiency.

In Fig. 4 the expected photocurrent density as a function of CdTe thickness, taking into account the volume recombination and the surface recombination at the back contact but neglecting reflection and the absorption losses in CdS, is shown.

Two limiting cases are considered. One is the case for zero recombination velocity at the back, and the other is for very high recombination velocity there. We have also included the experimental results reported by Wu et al. [2] and Compaan et al. [4] for high efficiency solar cells. Notice that we have assumed 4 μm for the electron diffusion length, but the results do not vary very much when this parameter changes from 1 to 10 μm. Notice also that NREL results imply good quality (CSVST) material with an intermediate recombination velocity at the back contact. However, the results reported by Compaan et al. [4] and

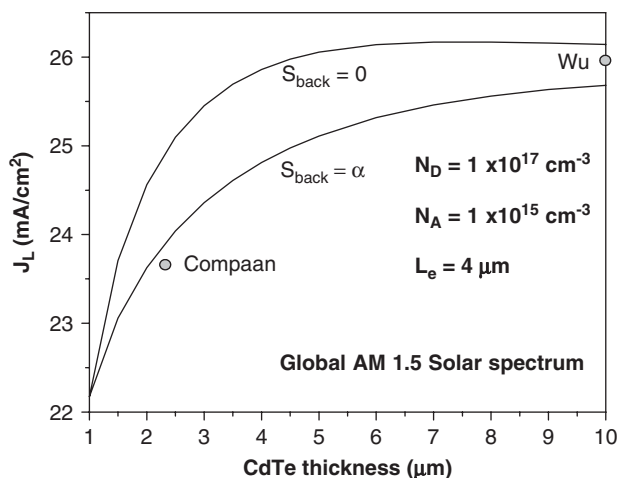


Fig. 4. Illumination current density (J_L) in CdS/CdTe solar cells as a function of the CdTe film thickness. Absorption and current generated in the CdS layer has been neglected. Two limiting cases were considered: no back surface recombination and very high recombination velocity at the back contact. In addition, two experimental points were included for reported high-efficiency solar cells by Wu et al. and Compaan et al. who made solar cells by RF-magnetron sputtering.

the results in this graph show that their material has not as good quality (smaller diffusion length) as Wu's since Compaan's group grow their CdTe films by sputtering.

From this graph we can have a better estimate for the optimum CdTe layer thickness. In this case, it seems that the smaller the back recombination velocity the smaller the required thickness for the CdTe layer. However, for high back recombination velocity, the optimum thickness is between 4 and 6 μm . The formation of a p^{++} region at the back for making the ohmic contact may help in reducing the surface recombination velocity there. In this case (low back surface recombination velocity), the optimum thickness for the CdTe layer would be around 4 μm .

Let us remember the experimental results for the highest-efficiency CdTe solar cells reported by Wu et al. [2] and compare with some of our calculations. We may see that a short circuit current density (J_{sc}) of 25.88 mA/cm^2 is around 94% of what ideally can be obtained from a 10 μm CdTe solar cell (see Fig. 3). Hence, it will be very difficult to improve this value. A maximum J_{sc} of 26 mA/cm^2 is expected, particularly if CdTe thickness is reduced slightly in order to improve the filling factor.

The measured open-circuit voltage of 845 mV is about 89% of the calculated built-in voltage. In order to improve this value we should dope both the CdS and CdTe layer for increasing majority carrier concentration at least one order of magnitude in each layer. By doing this we could expect that the open-circuit voltage could be increased to around 960 mV, around 100 mV more than the present values.

The present filling factor (0.755) is around 87% of the ideal filling factor for the measured open-circuit voltage. When this voltage is increased, the filling factor could become of the order of 0.79 being around 90% of the ideal one.

In other words, our realistic estimate for the maximum efficiency of CdS/CdTe cells is 17.6%, around 1% more than the present reported record efficiency, but this can be

achieved only by improving the open-circuit voltage and the filling factor of these solar cells. In order to do this we need to have some control on doping CdS and CdTe, and making better ohmic contacts to CdTe.

3. Conclusions

In summary, we have shown that the present record conversion efficiencies of CdS/CdTe solar cells are very close to the efficiency limit that can be achieved from this kind of hetero-junction cells. A higher short-circuit current density is not expected, but open-circuit voltage and filling factor can be improved achieving a maximum efficiency around 17.6%, i.e. 1% up from the current record. Our calculations also explain why the record efficiency has increased from 15.8% to only 16.5% during the last 10 years.

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