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# High-Efficiency CTO/ZTO/CdS/CdTe Polycrystalline Thin-Film Solar Cells

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## ABSTRACT

Cadmium telluride is a promising photovoltaic material for thin-film solar cells. However, the performance and reproducibility of devices has been limited by the conventional SnO<sub>2</sub>/CdS/CdTe device structure used for more than 30 years. In this paper, we report that the device performance and reproducibility of CdTe cells can be improved by using a modified CTO/ZTO/CdS/CdTe device structure developed at NREL. We achieved high FF of 77.34% and high J<sub>sc</sub> of near 26 mA/cm<sup>2</sup>, and fabricated a CdS/CdTe polycrystalline thin-film solar cell demonstrating an NREL-confirmed, total-area efficiency of 16.5%. This is the highest efficiency ever reported for CdTe solar cells.

## INTRODUCTION

Cadmium telluride has been recognized as a promising photovoltaic material for thin-film solar cells because of its near optimum bandgap of ~1.5 eV and its high absorption coefficient. Small-area CdTe cells with efficiencies of more than 15% [1] and commercial-scale modules with efficiencies of >10% [2] have been demonstrated. However, the performance and reproducibility of CdTe cells have been limited by the conventional SnO<sub>2</sub>/CdS/CdTe device structure that has been used for more than 30 years. For example, conventional transparent conductive oxides, primarily SnO<sub>2</sub> films, have an inherent sheet resistivity of ~10 Ω/Sq and an average transmission of 80%. This does not provide adequate design latitude when trying to optimize either device performance or manufacturing cost. The CdS window layer has a lower bandgap (~2.4 eV) that causes absorption in the short-wavelength region. Higher short-circuit current densities (J<sub>sc</sub>) can be achieved by reducing the CdS thickness to improve the blue response in the conventional CdS/CdTe device structure. However, reducing the CdS thickness can adversely impact device open-circuit voltage (V<sub>oc</sub>) and fill factor (FF). Finally, it is well known that the CdCl<sub>2</sub> treatment is important for making high-efficiency CdTe devices. However, one disadvantage of the CdCl<sub>2</sub>-treatment is that over-treatment can result in loss of adhesion. The adhesion problems can limit the optimal CdCl<sub>2</sub> treatment process, as well as device performance.

In the last five years, we have tried to understand and solve these issues related to conventional SnO<sub>2</sub>/CdS/CdTe device structure. We developed several novel materials and a modified CdTe device structure. First, we developed a novel process to prepare high-quality cadmium stannate (Cd<sub>2</sub>SnO<sub>4</sub>, or CTO) transparent conductive oxide (TCO) films, which have lower resistivity, higher transmittance and smoother surfaces than conventional SnO<sub>2</sub> TCO films [3-5]. When replacing the SnO<sub>2</sub> TCO film with a Cd<sub>2</sub>SnO<sub>4</sub> film in

a CdTe cell, J<sub>sc</sub> and FF of CdTe cells can both be improved [6-8]. Second, we developed and integrated the high-resistivity zinc stannate (Zn<sub>2</sub>SnO<sub>4</sub>, or ZTO) buffer layer into CdTe cells, which improved device performance and reproducibility [9-11]. Third, we developed and integrated modified CdS films with higher optical bandgap into CdTe devices. This improved blue quantum efficiency and J<sub>sc</sub>. Fourth, we developed a modified CTO/ZTO/CdS/CdTe device structure and made high-efficiency CdS/CdTe polycrystalline thin-film solar cells [12]. Finally, we developed a novel manufacturing process for fabricating high-efficiency CTO/ZTO/CdS/CdTe solar cells with potential for low cost and high throughput [13-14].

In this paper, we present the updated high-efficiency device results and give some examples to explain how the modified CTO/ZTO/CdS/CdTe device structure works for achieving the high performance and good reproducibility.

## EXPERIMENTAL

Both CTO and ZTO films were deposited by rf magnetron sputtering at room temperature in pure oxygen using commercial hot-pressed oxide targets. The CTO film was treated at 580°-660°C for 10-20 minutes in CdS/Ar atmosphere. The thickness of both CTO and ZTO films was varied from 100 to 300 nm. The CdS and CdTe films were prepared by chemical bath deposition (CBD) and close-spaced sublimation (CSS) techniques, respectively. The CdTe film was deposited at 570°-625°C for 3-5 minutes in O<sub>2</sub>/He mix atmosphere. After CdTe deposition, samples received a vapor CdCl<sub>2</sub> treatment at 400°-430°C for 15 minutes. CuTe:HgTe-doped graphite paste, followed by a layer of Ag paste, was then applied to the devices as the back-contact layer.

## UPDATED DEVICE RESULTS

### 1. High FF

Table 1 lists current-voltage parameters of two high-efficiency CdTe cells with FF of more than 77%. These are the highest FF values ever reported for CdS/CdTe polycrystalline thin-film solar cells. Device analyses from NREL and Colorado State University [15] indicate that these cells with high FF have lower series resistivity R<sub>s</sub> (~1 Ω cm<sup>2</sup>), higher shunt resistivity R<sub>sh</sub> (~3-5x10<sup>3</sup> Ω cm<sup>2</sup>), and better diode quality factor A (~2).

It is well known that reducing TCO resistivity is essential for reducing R<sub>s</sub> and improving FF in superstrate devices.

Table 1. NREL standard I-V measurements

Cell#	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	η (%)	Area (cm <sup>2</sup> )
W561-B	842.1	24.12	<b>77.26</b>	15.7	1.001
W562-B	848.1	23.97	<b>77.34</b>	15.7	0.976

We have reported previously that cadmium stannate TCO films have resistivities ( $\rho \sim 1.5 \times 10^{-4} \Omega \text{ cm}$ ) that are two to six times lower than  $\text{SnO}_2$  films [3-5]. It is thus obvious that by replacing the  $\text{SnO}_2$  with a CTO TCO film, the  $R_s$  can be reduced. Also, low-resistivity CTO films will allow us to increase the width of the sub-cell in modules, thereby increasing total-area module efficiency.

Integrating a ZTO buffer layer can significantly improve  $R_{sh}$  in two ways [9-11]. First, it reduces the probability of forming a localized TCO/CdTe junction with low  $V_{oc}$  and FF when the CdS film is thinned. Second, the ZTO buffer layer can act as an “etch-stop” layer during the back-contact formation process and greatly reduce shunting problems.

## 2. High $J_{sc}$

Table 2 lists I-V parameters of two high-efficiency CdTe cells with high  $J_{sc}$  of near  $26 \text{ mA/cm}^2$ .

Table 2. NREL standard I-V measurements

Cell#	$V_{oc}$ (mV)	$J_{sc}$ ( $\text{mA/cm}^2$ )	FF (%)	$\eta$ (%)	Area ( $\text{cm}^2$ )
W547-A	847.5	<b>25.86</b>	74.45	16.4	1.131
W567-A	845.0	<b>25.88</b>	75.51	16.5	1.032

In this work, high  $J_{sc}$ 's have been achieved by three ways: reducing  $J_{sc}$  loss due to TCO absorption, reducing  $J_{sc}$  loss due to CdS absorption, and reducing  $J_{sc}$  loss due to recombination in the junction and CdTe regions.

(1) We have reported previously that  $\text{Cd}_2\text{SnO}_4$  TCO film has higher transmittance and lower absorbance than  $\text{SnO}_2$  films [6-8]. Table 3 lists the  $J_{sc}$  loss due to TCO absorption for four different TCO films that are all deposited on Corning 7059 glass. It can be seen that the CTO film has the lowest  $J_{sc}$  loss ( $0.6 \text{ mA/cm}^2$ ) – two to four times lower than  $\text{SnO}_2$  films prepared by precursors TMT and  $\text{SnCl}_4$ , respectively. Also, we can see that integrating a ZTO buffer layer into a CdTe cell results in a  $J_{sc}$  loss of  $<0.1 \text{ mA/cm}^2$  due to its high bandgap and low absorption [9-11].

Table 3.

TCO	$R_s$ ( $\Omega/\text{Sq}$ )	$J_{sc}$ loss due to TCO absorption
$\text{SnO}_2$ ( $\text{SnCl}_4$ )	8-10	2.8
$\text{SnO}_2$ (TMT)	7-8	1.3
$\text{Cd}_2\text{SnO}_4$	7-8	0.62
CTO/ZTO	7-8/ $\sim 10^5$ - $10^6$	0.68

(2) In the conventional  $\text{SnO}_2/\text{CdS}/\text{CdTe}$  device, improved blue spectra response can be achieved by reducing the CdS thickness. However, reducing CdS thickness can impact device  $V_{oc}$  and FF, and reproducibility. In the CTO/ZTO/CdS/CdTe device, interdiffusion between the CdS and ZTO films “consumes” CdS film during device-fabrication. This interdiffusion can occur either at higher temperature ( $570^\circ$ - $650^\circ\text{C}$ ) in Ar, or at lower temperature ( $400^\circ$ - $420^\circ\text{C}$ ) in a  $\text{CdCl}_2$  atmosphere [10,12]. Therefore, we can control CdS consumption by optimizing CdTe deposition and  $\text{CdCl}_2$  treatment process. Using this technique has resulted in internal quantum efficiencies of  $>75\%$  at 400 nm and reduced  $J_{sc}$  loss due to CdS absorption to  $1.0$ - $1.3 \text{ mA/cm}^2$ . This property may also be exploited in production by using thicker CdS films, thereby enhancing yield without reducing  $J_{sc}$ .

(3) The interdiffusion between the CdS and ZTO layers also significantly improves the adhesion between the TCO and the CdS layer after  $\text{CdCl}_2$  treatment [10-12]. This improvement not only improves the device reproducibility, but also provides greater latitude in optimizing the  $\text{CdCl}_2$  treatment process. The time-resolved photoluminescence (TRPL) results indicate that an optimally  $\text{CdCl}_2$ -treated device has much longer TRPL lifetime, and thus, lower junction recombination. Indeed,  $J_{sc}$  loss due to recombination in the junction regions is only  $\sim 0.5 \text{ mA/cm}^2$ .

## 3. High efficiency

A number of CTO/ZTO/CdS/CdTe cells with efficiency of more than 15.8% have been fabricated. We have demonstrated a CTO/ZTO/CdS/CdTe polycrystalline thin-film solar cell with an NREL-confirmed total-area efficiency of 16.5% ( $V_{oc}=845.0 \text{ mV}$ ,  $J_{sc}=25.88 \text{ mA/cm}^2$ , FF=75.51%, and area= $1.032 \text{ cm}^2$ ). We believe that this is the highest efficiency ever reported for CdTe solar cells.

## CONCLUSIONS

The use of a modified CTO/ZTO/CdS/CdTe device structure can minimize some issues that are significant in conventional  $\text{SnO}_2/\text{CdS}/\text{CdTe}$  cells and can improve device performance and reproducibility. A CTO/ZTO/CdS/CdTe cell with an NREL-confirmed total-area efficiency of 16.5% has been achieved, which is the highest efficiency ever reported for CdS/CdTe solar cells.

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## REFERENCES

- [1] J. Britt and C. Ferekides, *Applied Physics Letters*, **62**, pp. 2851-2852 (1993).
- [2] H.S. Ullal et al., *Proc. 28<sup>th</sup> IEEE PVSC*, pp. 418-423 (2000).
- [3] X. Wu, W.P. Mulligan, and T.J. Coutts, *Thin Solid Films*, **286**, pp. 274-276 (1996).
- [4] T.J. Coutts, X. Wu, W.P. Mulligan, and J.M. Webb, *J Electronic Materials*, **25**, No. 6, pp. 935-943 (1996).
- [5] X. Wu and T.J. Coutts, U.S. Patent No. 6,221,495 (2001).
- [6] X. Wu, P. Sheldon, T.J. Coutts, D.H. Rose, W.P. Mulligan, and H.R. Moutinho, *Proc. of 14<sup>th</sup> NREL/SNL PV Program Review Meeting*, pp. 693-702, (1996).
- [7] X. Wu, P. Sheldon, T.J. Coutts, D.H. Rose, and H.R. Moutinho, *Proc. of 26<sup>th</sup> IEEE PVSC*, pp. 347-350 (1997).
- [8] X. Wu, T.J. Coutts, P. Sheldon, and D.H. Rose, U.S. Patent No. 5,922,142 (1999).
- [9] X. Wu, P. Sheldon et al, *Proc. of 15<sup>th</sup> NREL/SNL PV Program Review Meeting*, pp. 37-41 (1998).
- [10] X. Wu, S. Asher et al., *J Applied Physics*, **89**, No. 8, pp. 4564-4569 (2001).
- [11] X. Wu, P. Sheldon, and T.J. Coutts, U.S. Patent No. 6,169,246, (2001).
- [12] X. Wu, R. Ribelin et al., *Proc. of 28<sup>th</sup> IEEE PVSC*, pp. 470-474 (2000).
- [13] X. Wu and P. Sheldon, *Proc. of 16<sup>th</sup> European PVSEC*, pp. 341-344 (2000).
- [14] X. Wu and P. Sheldon, U.S. Patent No. 5,922,142 (1999).
- [15] C. Jenkins and J. Sites, Characterization report, (2001).