

Advances in CdTe R&D at NREL

X. Wu, J. Zhou, J.C. Keane, R.G. Dhere, D.S. Albin,
T.A. Gessert, C. DeHart, A. Duda, J.J. Ward, Y. Yan,
G. Teeter, D.H. Levi, S. Asher, C. Perkins,
H.R. Moutinno, B. To, K. Emery, T. Moriarty,
Y. Zhang, S. Wei, T. Coutts, and R. Noufi

*Presented at the 2005 DOE Solar Energy Technologies
Program Review Meeting
November 7–10, 2005
Denver, Colorado*

Conference Paper
NREL/CP-520-38954
November 2005

NREL is operated by Midwest Research Institute • Battelle Contract No. DE-AC36-99-GO10337



NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: <mailto:reports@adonis.osti.gov>

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



Advances in CdTe R&D at NREL

X. Wu, J. Zhou, J.C. Keane, R.G. Dhere, D.S. Albin, T.A. Gessert, C. DeHart, A. Duda, J.J. Ward, Y. Yan, G. Teeter, D.H. Levi, S. Asher, C. Perkins, H.R. Moutinho, B. To, K. Emery, T. Moriarty, Y. Zhang, S. Wei, T. Coutts, and R. Noufi

National Renewable Energy Laboratory, Golden, Colorado, email: xuanzhi_wu@nrel.gov

ABSTRACT

This paper summarizes the following R&D accomplishments at National Renewable Energy Laboratory (NREL): (1) Developed several novel materials and world-record high-efficiency CdTe solar cell, (2) Developed “one heat-up step” manufacturing processes, and (3) Demonstrated 13.9% transparent CdTe cell and 15.3% CdTe/CIS polycrystalline tandem solar cell.

Cadmium telluride has been well 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. Impressive results have been achieved in the past few years for polycrystalline CdTe thin-film solar cells at NREL. In this paper, we summarize some recent R&D activities at NREL.

1. 16.5%-Efficient Polycrystalline CdTe Thin-Film Solar Cell

The conventional SnO_2 /poly-CdS/poly-CdTe device structure, used for more than 30 years, has limited further improvements on performance and reproducibility of devices. In the past few years, we have attempted to understand issues related to the conventional device structure. And we have developed several novel materials and a modified device structure for minimizing these issues.

1.1 Cadmium Stannate (Cd_2SnO_4 or CTO) Transparent Conductive Oxide (TCO)

The CTO TCO films prepared by RF sputtering at room temperature have several advantages over conventional SnO_2 films. They have electrical resistivities ($\sim 1.5 \times 10^{-4} \Omega \text{ cm}$) two times and six times lower than SnO_2 films produced using a $\text{Sn}(\text{CH}_3)_4$ (TMT) and SnCl_4 chemistry, respectively. The high conductivity of the CTO films is attributed to its high mobility with high carrier concentration. CTO films also have significantly better optical properties than conventional SnO_2 films. This is, in part, due to the lower resistivities, which allow thinner film to be used. Our results have demonstrated that short-circuit current density (J_{sc}) can be improved by replacing the SnO_2 film with a CTO TCO film in CdTe cells.

1.2 High-Resistivity Zinc-Tin-Oxide (ZTO) Buffer Layer

The ZTO (ZnSnO_x) films were deposited by RF sputtering at room temperature. An as-grown ZTO film has a very high resistivity ($> 10^4 \Omega \text{ cm}$). After annealing at a higher temperature (540-620°C) for 3-5 minutes, the film resistivity is reduced to 1-10 $\Omega \text{ cm}$. The ZTO bandgap (E_g) remains the same (~ 3.6 eV), but its optical transmission is slightly improved. We also found that there is interdiffusion between the CdS and ZTO films. This interdiffusion can occur either at higher temperature (570-650°C) in Ar, or at lower temperature (400-420°C) in a CdCl_2 atmosphere. We have successfully applied the interdiffusion feature to minimize issues related to the conventional device structure and to improve device performance and reproducibility. The interdiffusion of the CdS and ZTO layers improved the quantum efficiency of a CdTe cell over the entire active wavelength region (400-860 nm).

1.3 Oxygenated Nanocrystalline CdS Window Layer

In a conventional CdTe device, a poly-CdS film has been used most commonly as a window material. But it has three main issues that limit device performance. First, a $\text{CdS}_{1-y}\text{Te}_y$ alloy with a lower bandgap can be formed between the CdTe and poly-CdS films, which degrades device performance. Second, poly-CdS has a bandgap of ~ 2.42 eV, which causes considerable absorption in the short-wavelength region. Third, there is a nearly 10% lattice mismatch between the poly-CdTe film and the poly-CdS film, which causes high defect density at the junction region.

We developed a novel window material, oxygenated nanocrystalline CdS film (nano-CdS:O), prepared at room temperature in an oxygen/argon gas mixture by RF magnetron sputtering. The CdS:O film has a higher optical bandgap (2.5-3.1 eV) than the poly-CdS film. The CdS:O films also have a nanostructure; the bandgap increases with an increase of oxygen content and the grain size decreases. The higher oxygen content present in the nanocrystalline CdS:O films can significantly suppress the Te diffusion from the CdTe into the CdS film and the formation of a $\text{CdS}_{1-y}\text{Te}_y$ alloy, which results in a higher quantum efficiency in the short-wavelength region and a higher J_{sc} . J_{sc} values of nearly 26 mA/cm^2 in a CTO/ZTO/CdS:O/CdTe cell are achieved by using the nanocrystalline CdS:O film.

1.4 CTO/ZTO/CdS/CdTe Device Structure and High-Efficiency CdTe Cells

Using novel materials and the modified device structure, we achieved a high FF of 77.3%, a high J_{sc} of nearly 26 mA/cm^2 , and an efficiency of 16.5% measured by NREL's standard current-voltage (I-V) measurement, which represents individual optimized cases. The best CTO/ZTO/CdS/CdTe polycrystalline thin-film solar cell has an NREL-confirmed total-area efficiency of 16.5% (open-circuit voltage $[V_{oc}] = 845.0$ mV, $J_{sc} = 25.88$ mA/cm^2 , FF=75.51%, and area=1.032 cm^2). This is the highest efficiency for a CdTe-based polycrystalline thin-film solar cell.

1.5 V_{oc} Improvement

To achieve CdTe cells with an efficiency of 18%-20%, our research focused on improving the ratio of V_{oc}/E_g to at least 60% ($V_{oc} \sim 900$ mV). This could be achieved in three ways: (1) improve the built-in potential by minimizing compensation and increasing doping of the CdTe film; (2) improve the diode quality A-factor by minimizing the recombination-center density in the junction region; and (3) reduce the back-contact barrier height. We have achieved an NREL-confirmed V_{oc} of 858 mV in a CdTe cell with an efficiency of 15.6% by optimizing the device process and back contact. Our research also focuses on the study of defects, which limit doping of CdTe films.

2. Novel Manufacturing Processes

Commercial-scale CdTe modules with efficiencies of 6%-9% were produced by several CdTe deposition techniques, and they have demonstrated the ability to attract production-scale capital investments. However, there are undesirable issues in the conventional CdTe module manufacturing processes. First, further improvement of the performance and yield of CdTe modules has been limited by the use of the conventional SnO_2 /poly-CdS/poly-

CdTe device structure. For example, a thicker CdS layer has to be used for maintaining high yield, which also results in low J_{sc} and low efficiency. Second, the conventional processes include time-consuming and expensive heat-up and cool-down segments that limit throughput and yield, and some “wet” processes that generate a large amount of liquid waste. To apply our high-efficiency CdTe cell fabrication technique, we developed novel manufacturing processes for minimizing these issues and producing high-efficiency CdTe modules.

Conventional soda-lime (SL) glass is well known to have poorer properties than borosilicate glass, such as a higher thermal expansion coefficient, higher Na and Fe content, higher absorbance, and lower softening temperature. Also, commercial SnO_2 TCO films have an inherent sheet resistivity of $\sim 10\text{-}15 \Omega/\square$ and an average transmission of $\sim 80\%$, which is not good enough to improve CdTe cell performance. However, the inexpensive attribute of commercial SnO_2/SL -glass makes it benign for manufacturing practice. Based on SnO_2/SL -glass substrates, integrating a ZTO buffer layer developed at NREL improves the performance and reproducibility of CdTe cells. The J_{sc} values of CdTe cells were also improved greatly by using nano-CdS:O film developed at NREL. Both the ZTO film and the CdS:O film are prepared by RF magnetron sputtering at room temperature. The entire process is managed to contain only one heat-up segment.

Due to the lower softening temperature of commercial SnO_2/SL -glass substrate, CdTe deposition must be performed at temperatures below 570°C . The process of lowering the CdTe deposition temperature impacts the structural properties and density of the CdTe films. Therefore, the deposition parameters in the close-spaced sublimation (CSS) process have been optimized to obtain high-quality and denser CdTe films. Using the developments mentioned above, we have fabricated a number of CdTe cells on commercial Tek 15 SnO_2/SL -glass (produced by LOF) with NREL-confirmed efficiencies of more than 14%. The best cell has an efficiency of 14.4% ($V_{oc}=829.3 \text{ mV}$, $J_{sc}=23.48 \text{ mA/cm}^2$, and $\text{FF}=74.07\%$). This process also demonstrated better uniformity, which can help to reduce the efficiency gap between small-area cells and modules.

In summary, the novel manufacturing processes provide attractive alternatives for producing CdTe modules with a potential of high throughput and low cost by (1) increasing device efficiency, (2) improving device yield, and (3) simplifying the device fabrication process. We have transferred these techniques to our main industrial partners, which may help them to improve efficiency and yield of CdTe modules.

3. 13.9%-Efficient Transparent CdTe Thin-Film Solar Cell with an Infrared Transmission above 50%

To move thin-film solar-electric technology forward in the next 10 years, the U.S. DOE NCPV High Performance PV Project has selected polycrystalline tandem thin-film solar cells to advance the state-of-the-art efficiency to 25%. In this polycrystalline thin-film tandem cell project, the most critical issue is to make a high-efficiency top cell ($>15\%$) with a high bandgap ($E_g=1.5\text{-}1.8 \text{ eV}$) and high transmittance ($T>70\%$) in the near-infrared (NIR) wavelength region, because the top cell contributes more than two-thirds of the power to a two-junction device. Several high-bandgap alloys based on I-III-VI and II-VI compounds, such as CuGaSe_2 (CGS), Cu(InGa)(SeS)_2 (CIGSS), Cu(InGa)S_2 (CIGS), CuInS_2 , and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ (CZT), with efficiency of $\sim 12\%$ are being investigated. However, when the CGS and CZT cells have the necessary transparent back-contact, the device efficiencies decrease to less than 7%. CdTe is also a good candidate for the top cell, because CdTe efficiencies of more than 16% have been demonstrated.

To qualify CdTe as a top cell, the first challenge is to replace the opaque back-contact with a transparent one. In the past, almost all R&D activities in this area focused on developing a transparent back-contact with E_g larger than the E_g of the top cell, such as ZnTe:Cu or ZnTe:N with E_g of $\sim 2.26 \text{ eV}$, or ITO with E_g of $\sim 3.9 \text{ eV}$. The best result is a 10.1%-efficient CdTe cell with a ZnTe:Cu back-contact that has a 60%-85% film transmission in the NIR region.

In our work, we exploited a different approach involving the use of a thin, low- E_g back-contact material, Cu_xTe with E_g of $<1.08 \text{ eV}$, which is lower than the E_g of the CdTe absorber film, to achieve high transparency in the NIR wavelength region. We developed a novel three-step process for producing the Cu_xTe contact, which includes the following: (1) produce a Te-rich layer by chemical etch; (2) deposit thin Cu (or Cu alloy); and (3) post-heat anneal to form Cu_xTe layer. Using the ultra-thin Cu_xTe back-contact with the novel materials used in the high-efficiency CdTe cell process, we fabricated a number of CTO/ZTO/nano-CdS:O/CdTe/ Cu_xTe /ITO/Ni-Al grid cells with efficiencies of more than 13.5% by this technique. The best cell has an NREL-confirmed, total-area efficiency of 13.94% ($V_{oc}=806.1 \text{ mV}$, $J_{sc}=24.97 \text{ mA/cm}^2$, $\text{FF}=69.22\%$, and $\text{area}=0.41 \text{ cm}^2$) with $\sim 60\%$ - 40% transmission in the wavelength range of 860-1300 nm. We have also made several mechanically stacked, four-terminal CdTe/CIS tandem cells. A CdTe/CIS polycrystalline thin-film tandem cell with an NREL-confirmed total-area efficiency of 15.3% was achieved, exceeding the FY 2006 milestone (15%) in DOE/NCPV's High Performance PV Project.

4. Conclusions

The recent accomplishments of NREL's CdTe research group have been summarized in the following aspects:

- (1) Developed several novel materials, including CTO TCO, ZTO buffer layer, and nanocrystalline CdS:O window layer, and a modified CdTe device structure. Demonstrated a CTO/ZTO/CdS/CdTe cell with an NREL-confirmed total-area efficiency of 16.5%.
- (2) Developed “one heat-up step” manufacturing processes on either high-temperature glass or commercial SL/ SnO_2 substrates, which provide an attractive alternative for producing CdTe modules with high efficiency, high throughput, and low cost.
- (3) Demonstrated an NREL-confirmed total-area 13.9%-efficient CTO/ZTO/nano-CdS:O/CdTe/ Cu_xTe cell with more than 50% NIR transmission, and a 15.3%-efficient CdTe/CIS mechanically stacked tandem cell.

ACKNOWLEDGEMENTS

This work is supported by the U.S. Department of Energy under Contract No. DE-AC36-99GO10337 to NREL.

MAJOR FY 2005 PUBLICATIONS

- X. Wu, “High-efficiency polycrystalline CdTe thin-film solar cells,” *Solar Energy*, 77, 2004, p803.
- X. Wu and J. Zhou, “High-efficiency CdTe solar cells on commercial $\text{SnO}_2/\text{soda-lime}$ glass prepared by novel manufacturing process,” *Proc. of the 19th European PVSEC*, 2004, p1721.
- X.Wu, J. Zhou, A.Duda, J. Keane, T.A. Gessert, Y. Yan, and R. Noufi, “13.9%-efficient CdTe polycrystalline thin-film solar cells with an infrared transmission of $\sim 50\%$,” *PV in Progress*, 2005, in press.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services and Communications Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE (DD-MM-YYYY) November 2005		2. REPORT TYPE Conference Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Advances in CdTe R&D at NREL			5a. CONTRACT NUMBER DE-AC36-99-GO10337		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) X. Wu, J. Zhou, J.C. Keane, R.G. Dhere, D.S. Albin, T.A. Gessert, C. DeHart, A. Duda, J.J.Ward, Y. Yan, G. Teeter, D.H. Levi, S. Asher, C. Perkins, H.R. Moutinno, B. To, K. Emery, T. Moriarty, Y. Zhang, S. Wei, T. Coutts, and R. Noufi			5d. PROJECT NUMBER NREL/CP-520-38954		
			5e. TASK NUMBER PVA6.4301		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393				8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-520-38954	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S) NREL	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER	
12. DISTRIBUTION AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT (Maximum 200 Words) This paper summarizes the following R&D accomplishments at National Renewable Energy Laboratory (NREL): (1) Developed several novel materials and world-record high-efficiency CdTe solar cell, (2) Developed "one heat-up step" manufacturing processes, and (3) Demonstrated 13.9% transparent CdTe cell and 15.3% CdTe/CIS polycrystalline tandem solar cell. Cadmium telluride has been well 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. Impressive results have been achieved in the past few years for polycrystalline CdTe thin-film solar cells at NREL. In this paper, we summarize some recent R&D activities at NREL.					
15. SUBJECT TERMS Photovoltaics; solar; CdTe; PV; NREL					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code)