

Advances in CdTe R&D at NREL

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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 SnO₂/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 (Cd₂SnO₄ or CTO) Transparent Conductive Oxide (TCO)

The CTO TCO films prepared by RF sputtering at room temperature have several advantages over conventional SnO₂ films. They have electrical resistivities ($\sim 1.5 \times 10^{-4}$ Ω cm) two times and six times lower than SnO₂ films produced using a Sn(CH₃)₄ (TMT) and SnCl₄ 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 SnO₂ 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 SnO₂ 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 ($>10^4$ Ω cm). After annealing at a higher temperature (540-620°C) for 3-5 minutes, the film resistivity is reduced to 1-10 Ω 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 CdCl₂ 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 CdS_{1-y}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 CdS_{1-y}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/cm² 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/cm², 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/cm², FF=75.51%, and area=1.032 cm²). 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 SnO₂/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% ($V_{oc}=829.3\ \text{mV}$, $J_{sc}=23.48\ \text{mA}/\text{cm}^2$, 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), $\text{Cu}(\text{InGa})(\text{SeS})_2$ (CIGSS), $\text{Cu}(\text{InGa})\text{S}_2$ (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 $\text{ZnTe}:\text{Cu}$ or $\text{ZnTe}:\text{N}$ 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 $\text{ZnTe}:\text{Cu}$ 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% ($V_{oc}=806.1\ \text{mV}$, $J_{sc}=24.97\ \text{mA}/\text{cm}^2$, $\text{FF}=69.22\%$, 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.

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- 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.

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