Polycrystalline Thin-Film Multijunction Solar Cells


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ABSTRACT

We present a digest of our research on the thin-film material components that comprise the top and bottom cells of three different material systems and the tandem devices constructed from them.

1. Objectives

Develop approaches toward improving transparent top cells, and an appropriate bottom cell to demonstrate a 25%-efficient polycrystalline thin-film tandem solar cell.

2. Technical Approach

We focused on three areas of exploration:

• Top cell: Three material systems to be evaluated, CGS, CdTe, and CdMgTe. The top cell is the more-critical component in a dual-junction tandem cell, expected to deliver about two-thirds of the power.

• Bottom cell: Optimize the CIS device (bandgap $E_g \sim 1$ eV) as a bottom cell, with emphasis on red response.

• Available choices for interconnecting the top and bottom cell: Assess the performance of the different components in a dual-junction thin-film device.

3. Salient Results

We provide salient results for the three top cell materials, and one bottom-cell material.

3.1 Top Cell

A. CdTe-based top cell

We have shown previously through modeling that it is possible to achieve a 25% all-thin-film dual-junction tandem device by using a top-cell bandgap in the range of 1.5 to 1.8 eV, where 1.7 eV is optimum. In the short term, this allows us to use a transparent CdTe-based cell as the top cell, with a 15% CIS bottom cell.

In the study of thin CdTe cells and transparent CdTe cells, we found that the conventional graphite paste or ZnTe:Cu back-contact are not suitable for device fabrication of thin CdTe or transparent CdTe cells. We developed a novel three-step process for producing a Cu$_x$Te back-contact, which includes: (1) produce a Te-rich layer by chemical etch, (2) deposit thin Cu (or Cu alloy), and (3) post-heat anneal to form Cu$_x$Te layer. We also tried to understand the following: (1) the stoichiometry of Cu$_x$Te film prepared by the three-step process, (2) Cu$_x$Te thickness control and its effect on device performance, (3) Cu$_x$Te phase control and its effect on device performance, and (4) stability of Cu$_x$Te back-contact with different thickness and phase.

We have successfully applied a Cu$_x$Te back-contact to fabricate a high-efficiency transparent CdTe cell as a top cell in a four-terminal tandem solar cell. 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 $\sim 2.26$ eV, or ITO with $E_g$ of $\sim 3.9$ 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 near-infrared (NIR) region. However, we exploited a thinner Cu$_x$Te back-contact and modified device structure to fabricate high-efficiency poly-CdTe thin-film solar cells with higher NIR transparency. We fabricated several CTO/ZTO/nano-Cd$S_2$:O/CdTe/Cu$_x$Te/ITO/Ni-Al grid cells with efficiencies of more than 13% by this technique. The best cell has an NREL-confirmed, total-area efficiency of 13.94% ($V_{oc} = 806.1$ mV, $J_{sc} = 24.94$ mA/cm$^2$, FF = 69.22%, and area = 0.41 cm$^2$) with $\sim 60$%–40% transmission in the wavelength range of 860–1300 nm. We also produced a CdTe/CIS polycrystalline thin-film tandem cell with an NREL-confirmed total-area efficiency of 15.3%, exceeding the FY 2006 milestone in DOE/NREL’s HiPerf PV project.

B. CGS-based top cell

We measured a new total-area record efficiency of 10.23% for modified CuGaSe$_2$ solar cells. This improvement resulted from a modified three-stage growth process of the absorber layer, with more Cu-rich conditions in the second stage and the addition of $<1$% of In at the end of the third stage. This modified growth resulted in higher current density and better quantum efficiency in the 10.23% cell, and may have made the surface of the modified CGS absorber similar to that of CIGS. The density of surface defects in the modified CGS cell is lower than that in the 9.53% cell. The modified CGS has a stronger (220/204) preferred orientation in the bulk, compared to that in the 9.53% CGS. We observed a Cu-depleted surface layer within the top part of the 10.23% modified CGS film, with composition close to that of the Cu$_x$(In,Ga)$_3$Se$_5$ phase. The best 4-terminal tandem...
device using CGS/SnO₂ as a top cell and CdS/CIS as a bottom cell gave an efficiency of 9.7% with \( V_{oc} = 1.29 \) V.

C. CdMgTe-based top cell

CdMgTe thin films are a new candidate for a top cell. The Cd₁₋ₓMgₓTe alloy system has several advantages: (1) large range of energy gap that allows material in the 1.6–1.8-eV range, with the least amount of Mg addition (5%–25%), (2) least deviation from the lattice constant of CdTe (tetrahedral radius, CdTe = 2.81 Å, MgTe = 2.76 Å), and (3) linear variation of bandgap with Mg. The limited amount of work done on these alloys has not explored them for polycrystalline thin films. A number of approaches were tried for depositing these alloys. Co-deposition using CdTe and MgCl₂, deposition from pre-alloyed Cd₁₋ₓMgₓTe source material, and co-deposition of CdTe and MgF₂ were attempted, but were unsuccessful. We succeeded when we co-deposited CdTe and Mg. We were able to vary the composition over a wide range by adjusting the relative rates of deposition of the two sources. Figure 1 shows the dependence of the energy gap on the Mg content. A linear relationship is observed, and the regression fit can be describe by: \( E_g = 1.54 \times + 1.1 \) eV.

3.2 Bottom Cell

To date, we have leveraged the optimization of the performance of CIGS-based solar cells carried out under the polycrystalline thin-film CIGS project to improve the efficiency of the CuInSe₂-based device (1 eV) used as the bottom cell for two-junction tandems. We demonstrated a 15.1% solar cell. At this point, the performance is maximized for the objective of this project; therefore, we will shift some of the effort to enhance improvement to the CGS (1.7 eV) top cell.

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![Fig. 1. Energy gap as a function of Mg content for Cd₁₋ₓMgₓTe alloy thin films.](image)
# Polycrystalline Thin-Film Multijunction Solar Cells

**Abstract**

We present a digest of our research on the thin-film material components that comprise the top and bottom cells of three different material systems and the tandem devices constructed from them.

**Subject Terms**

- Photovoltaics; solar; polycrystalline; thin film; multijunction solar cell; PV; NREL