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# Polycrystalline CdTe photovoltaics with efficiency over 18% through improved absorber passivation and current collection

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ABSTRACT

Sublimated thin-film CdTe photovoltaic devices with conversion efficiencies over 18% and a fill-factor greater than 79% have been repeatedly obtained using high-rate fabrication processes on commercial soda-lime glass substrates used in CdTe modules. Four major improvements to the device have enabled an increase in efficiency from a baseline of approximately 12–18.7%: 1) A sputtered multilayer metal-oxide anti-reflection layer; 2) total replacement of the CdS window layer with a higher bandgap sputtered $Mg_xZn_{1-x}O$ (MZO) window layer; 3) deposition of the CdTe layer at a higher thickness and substrate temperature; and 4) an evaporated tellurium back-contact. This work describes the effect of these changes on the device performance and film microstructural characteristics using various methods. Multiple devices with comparable high efficiency have been fabricated and demonstrated using methods described in this study, yielding very high efficiencies for CdTe polycrystalline thin-film photovoltaics using deposition processes and equipment in a university setting.

## 1. Introduction

Thin-film CdTe photovoltaics have consistently demonstrated the lowest cost solar electricity generation, particularly for utility scale applications. CdTe is a *p*-type absorber that has a bandgap of 1.5 eV which is nearly optimal for photovoltaic conversion. Approximately 2 μm is sufficient to absorb most of the visible solar spectrum [1,2]. CdTe films are typically deposited on glass substrates using low-cost hardware and high-rate deposition processes [3–5] reducing production costs. Typical crystalline silicon photovoltaics require wafers that are 150–200 μm thick and use a more complex and capital-intensive fabrication process [3].

The low-cost manufacturing of thin-film CdTe PV has enabled agreement for a record low cost power purchase agreement of ¢3.8/kWh for a 100 MW field [6], which is significantly lower than the average cost of electricity in the U.S. of ¢11/kWh [7]. With recent improvements, research-scale small devices have recorded efficiencies of 22.1% [8], while modules with up to 18.6% [9] efficiency have been produced. The leading CdTe PV manufacturer, First Solar Inc., has increased *average production module* efficiency from 13.5% in the first quarter of 2014 [10] to 16.7% in the first quarter of 2017 [11]. Further improving the efficiency without substantial increase in production cost will reduce the levelized cost of energy for CdTe photovoltaics [12,13].

Maintaining the dual requirement of high efficiency and low cost requires the use of film deposition techniques suitable for mass production of millions of solar modules per year. The vapor deposition methods used for this study, including sublimation, evaporation, and sputter deposition, have been used in large scale manufacturing for solar and other industries. Commercially available 3.2-mm soda-lime glass with a fluorine-doped tin-oxide (FTO) transparent conducting layer is a standard substrate for thin-film PV manufacturing, including for CdTe, due to its sufficient strength, reliability, and low cost. Using processes suitable for large scale manufacturing, the authors have explored new materials and process modifications to systematically reduce conversion losses in devices fabricated on low cost glass substrates. This has resulted in an 18.3% efficient device which has been externally certified by Newport Corporation PV Laboratory, Bozeman, Montana, U.S.A. [14]. These independent measurements correspond closely to internal measurements performed at Colorado State University. The performance results have been repeatedly replicated. This is one of the highest efficiency device for which the complete structure has been reported in detail. A detailed materials characterization protocol was used to guide the process optimization. Methods include transmission electron microscopy (TEM) and energy dispersive X-ray

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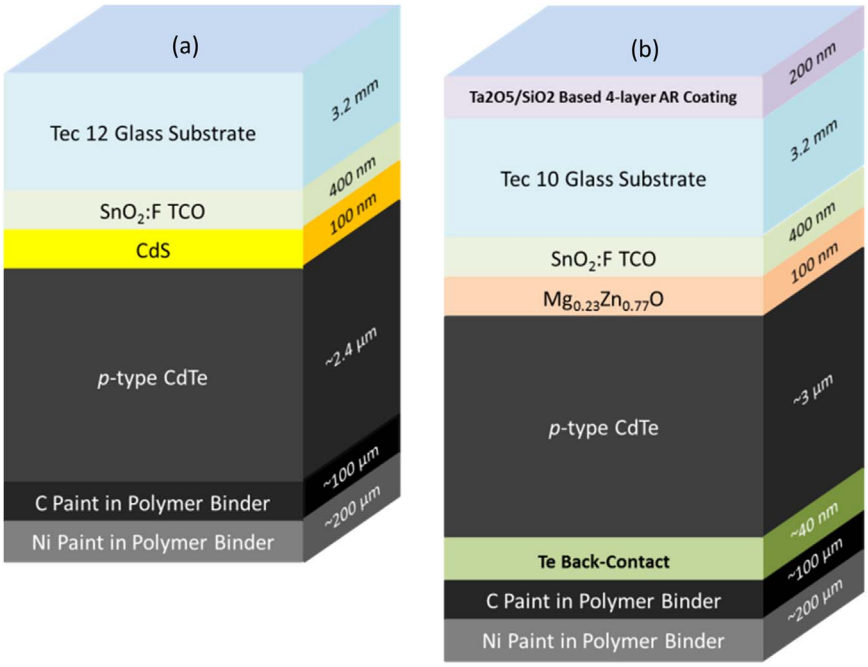


**Fig. 1. Schematic of** (a) CdS/CdTe baseline device (b) device with changes incorporated to achieve high efficiency (not to scale).

spectroscopy (TEM-EDS). Electrical characterization includes current density-voltage (J-V) measurements to derive device efficiency parameters and spectral response measurements.

## 2. Device structure for improved efficiency

Thin-film CdTe device structure and processing improvements were characterized to understand their impact on performance and microstructure. At the start of the study, baseline device efficiency was typically 12%, with the device's structure shown in Fig. 1(a). This device had a traditional structure with CdS as the *n*-type window layer while CdTe was the *p*-type absorber. Using CdS as the window layer has a major drawback. CdS is a strong absorber of light above its bandgap of 2.4 eV, and thus the light absorbed within this layer cannot reach the CdTe absorber layer.[15] Photogenerated carriers from CdS are not collected and the light absorbed in this layer is wasted, limiting short-circuit current density ($J_{SC}$) in the baseline devices. To overcome this limitation, a high band-gap MgZnO (MZO) buffer layer was introduced to replace the CdS window layer. In addition to the traditional Cu back-contact formation, a 20 nm Te layer was also introduced to improve the back-contact. The deposition temperature, film thickness and passivation conditions for CdTe absorber were optimized to achieve improved device performance. At the conclusion of this study, the device structure had been significantly modified, as shown in Fig. 1(b). This improved structure, combined with optimized CdTe absorber deposition and passivation conditions, resulted in the increased device performance of over 18%. Fabrication conditions and characterization of these devices are extensively described in subsequent sections.

## 3. Experimental

To understand the changes in the optimized new fabrication process, it is important to overview the fabrication of the baseline device shown in Fig. 1(a). The baseline devices were fabricated using a vacuum deposition system at Colorado State University (CSU) capable of performing processes in-line to fabricate a nearly complete CdTe solar cell [16]. The substrate used for the CdS/CdTe reference devices (Fig. 1a) was NSG TEC 12D soda-lime glass produced by Pilkington Group Limited. The NSG TEC 12D glass had fluorine doped tin oxide (FTO) followed by an un-doped, high resistivity transparent (HRT) layer deposited by the glass manufacturer. This HRT layer deposited by glass manufacturer on the TCO was un-doped tin oxide. Only reference devices were fabricated using TEC12D glass while all other devices in this study were deposited on TEC10 glass. Prior to thin-film deposition, the glass substrates were cleaned using International Products Corporation's Micro-90 cleaning solution followed by ultrasonic cleaning and drying under methanol vapor. The baseline device (Fig. 1(a)) fabrication process began with the preheating of the substrate, followed by 130 nm of *n*-type CdS and 2.4 µm of CdTe deposition at a substrate temperature of 440 °C and 445 °C, respectively [16]. After CdTe deposition, sublimation of a $CdCl_2$ layer and an annealing treatment at approximately 400 °C comprised the passivation process for the CdTe absorber. The $CdCl_2$ material was 99.996% pure and Cu content for the material was less than 1 ppm. The substrate was then removed from the in-line vacuum chamber, rinsed with deionized water, and heated again under 40 mTorr vacuum to approximately 150 °C using the in-line fabrication system [16]. A small amount of CuCl was then sublimed onto the CdTe for 110 s with CuCl source temperature at 190 °C and annealed at 200 °C for 220 s to form the device back contact. 99.99% pure copper(I) chloride manufactured by Aldrich-ADL was used and processes was performed under 40 mTorr vacuum with ultrahigh purity nitrogen as the career gas. The back electrode of this device consisted of carbon- and nickel-containing acrylic paints.

Use of HRT layers has been studied to enable the use of thinner CdS layers to decrease above bandgap absorption, but some CdS is still needed to maintain voltage [15]. The CdS *n*-type window layer is a strong absorber of blue light, which causes lack of absorption in the CdTe absorber. Using a more transparent window layer would lead to greater absorption of light in the CdTe absorber layer and higher current generation. MZO has a bandgap of 3.7 eV that is higher than CdS bandgap, which greatly reduces parasitic window layer absorption. ZnO alloyed with MgO to form a HRT layer has been studied by Kephart et al. [17]. In addition to increased ultraviolet transmission, MZO provides a band-alignment more suitable for CdTe [15,17]. The MZO with a composition of $Mg_{23}Zn_{77}O$ was used without an *n*-type CdS window layer to achieve both higher $J_{SC}$ and open-circuit voltage ($V_{OC}$). All devices fabricated using MZO buffer layers were deposited on NSG TEC 10 soda lime glass that had FTO coated by the manufacturer as the transparent conducting oxide (TCO). TEC 10 glass did not have an un-doped tin oxide HRT layer deposited on FTO. 100 nm MZO films were