

High efficiency ultra-thin sputtered CdTe solar cells

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Abstract

Large scale manufacturing of CdTe PV modules at the GW/yr level may be constrained due to the limited availability of the relatively rare (Te) element and the volume of potentially hazardous (Cd) material being used in the typically 3–8 μm thick CdTe absorber layer. However, we find that it is possible to reduce the CdTe layer thickness without much compromise in efficiency. The CdS/CdTe solar cells were fabricated using magnetron sputtering with ultra-thin CdTe layers in the range of 0.5–1.28 μm . The ultra-thin films and cells were characterized using X-ray diffraction (XRD), optical transmission, scanning electron microscopy (SEM), current–voltage and quantum efficiency measurements. These results were compared with those of standard 2.3 μm thick CdTe sputtered cells. Different post-deposition processing parameters were required for cells with ultra-thin and standard CdTe thicknesses to achieve high efficiency. Ultra-thin CdTe cells showed crystallographic texture and $\text{CdTe}_{1-x}\text{S}_x$ alloy formation after CdCl_2 treatment very similar to standard CdTe cells. Optimization of the post-deposition CdCl_2 treatment and back-contact processing yielded cells of 11.2% efficiency with 0.7 μm CdTe compared to 13.0% obtained with standard 2.3 μm CdTe cells. © 2006 Elsevier B.V. All rights reserved.

Keywords: CdTe cells; Ultra-thin CdTe; Solar cells; Polycrystalline solar cells

1. Introduction

The booming photovoltaic market in Japan, Europe and the US is about to cause a significant reduction in single crystal based PV industry growth [1,2] due the shortage and increased costs of PV-grade silicon feed stock which has traditionally depended heavily on reject or waste Si from the semiconductor industry. This provides a major opportunity for growth of the polycrystalline thin-film-based PV industry. Among available thin-film solar

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cell (α -Si, CuInGaSe₂ and CdTe) materials, CuInGaSe₂ has some drawbacks due to limited availability and increasing cost of indium. While α -Si does not have any problem of raw material availability, the slow deposition rate of the semiconductor layers is a disadvantage in the competition. Cadmium telluride (CdTe) may be the strongest candidate for high throughput, large-scale manufacturing [3] of polycrystalline thin-film solar cells. Because of its high absorption coefficient ($>1 \times 10^4 \text{ cm}^{-1}$) and direct band-gap (1.5 eV), about 1 μm thick CdTe film is enough for absorption of $\sim 90\%$ of photons with energy higher than its bandgap. However, the best efficiency (14–16.5%) solar cells have been reported using much thicker CdTe layers [4,5]. At $\sim 3 \mu\text{m}$ of CdTe absorber, the availability of elemental Te may be a concern if production levels increase above 20 GW per year [6]. The development of cells with a much thinner CdTe layer ($<1 \mu\text{m}$, which we call ultra-thin) would help to extend Te supplies and would have additional advantages in manufacturing such as reduced materials cost, higher throughput, easier cell isolation and interconnections, lower use of toxic materials and reduced waste treatment cost.

Using realistic cell parameters [7], the efficiency of a polycrystalline thin-film solar cell is predicted to reach $\sim 25\%$ in a two-junction tandem solar cell configuration such as shown in Fig. 1. Current matching requires that the optimum bandgap of the top cell in such a double-junction solar cell is 1.6–1.8 eV. However, the fabrication of such a top cell with high efficiency has been very difficult so far [8–11]. An alternative approach to achieving current matching is to use an ultra-thin CdTe cell for the top cell to allow some above-band-gap photons to enter the bottom cell. Fig. 2 illustrates that higher transmission occurs for both below- and above-band-gap photons in such ultra-thin cells. Thus, ultra-thin CdTe cells have an additional application as a candidate for the top cell in two-junction tandem solar cells.

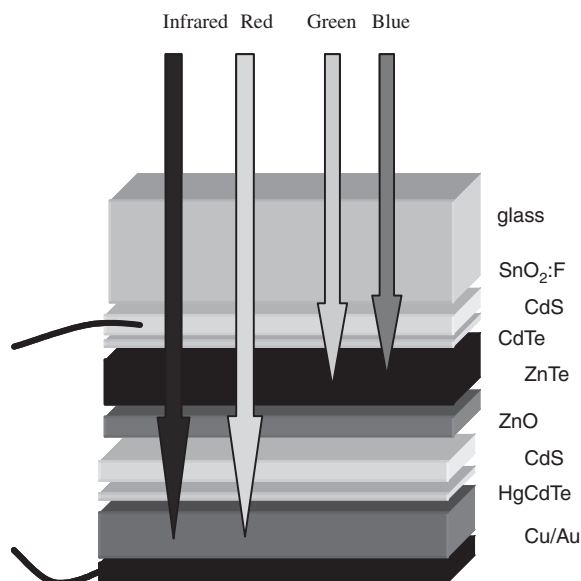


Fig. 1. Superstrate type, two-junction, two-terminal tandem cell structure based on CdTe and HgCdTe absorbers for top and bottom cells, respectively.

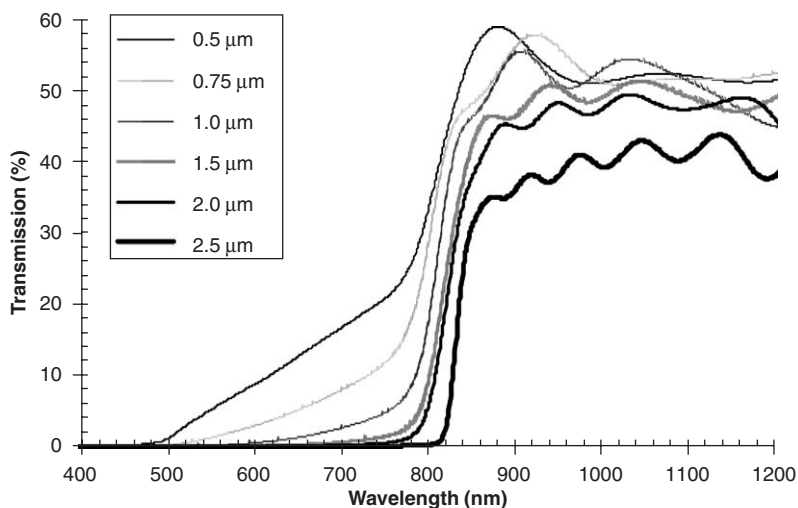


Fig. 2. Transmission of cells with different CdTe thicknesses.

In an earlier study, we observed that when all other processing parameters are held constant at standard conditions while decreasing the CdTe thickness from 3.0 to 0.5 μm , the efficiency decreased from $\sim 12\%$ to 5% [12]. The decrease in efficiency was not only due to the expected loss in J_{SC} because of reduced photon collection in the red. An even larger decrease arose from a drop in V_{OC} . In this paper, we report the effect of a first-order reoptimization of processing conditions for ultra-thin CdS/CdTe solar cells and the achievement of improved efficiency ultra-thin CdTe cells.

2. Experimental

In the current study, both CdS and CdTe films were deposited at $\sim 260^\circ\text{C}$ on commercial $\text{SnO}_2:\text{F}$ coated 3 mm thick soda-lime glass (Pilkington TEC-7) using planar magnetron sputtering. The optimized thicknesses of the CdS and CdTe layers in our standard sputtered cells are 0.13 and 2.3 μm , respectively [13]. The CdTe thickness in the present study was varied from 0.6 to 1.28 μm . The $\text{SnO}_2/\text{CdS}/\text{CdTe}$ cell structures were treated in vapors of CdCl_2 at $\sim 390^\circ\text{C}$ in dry air for various durations. The cells were then completed either with an evaporated Cu + Au bilayer or a Au-only layer back contacts through a mask to produce 0.15 cm^2 area dot cells followed by diffusion in room air at 150°C .

3. Results and discussion

Both of the two main post-deposition processes (CdCl_2 treatment duration and back contact diffusion) plausibly require reoptimization for thin CdTe structures. The CdCl_2 treatment duration and details of the back contact processing may depend on the amount of semiconductor material (i.e., thickness) in the cell structure. In fact, we showed in Ref. [14] from high angle X-ray diffraction (XRD) that chloride processing produces the usual intermixed alloy layer of CdSTe more quickly in the cells with thin CdTe. The use of

our standard 30 min CdCl_2 treatment at 387°C resulted in a thicker alloyed layer that was detrimental to cell performance. Thus, we found that the optimum treatment time occurred at about 10 min.

Line-of-sight transmission spectra also showed the sharpening of the absorption edge that has been seen in cells or films with $\sim 2.3\ \mu\text{m}$ of CdTe. However, the edge sharpening occurred after only 10 min of treatment at 387°C . In addition, the transmission for photon energies less than the band gap was somewhat improved after 10 min of treatment (compared with the transmission through cells with $2.3\ \mu\text{m}$ of CdTe) but deteriorated somewhat after 30 min of treatment. We attribute the decreased transmission with additional chloride treatment time to the increased surface roughness of these (over-treated) films. Again the regrowth and interdiffusion appear to proceed more rapidly for the CdS/CdTe films with thin CdTe.

The evaporated Cu/Au back contact structure used with our sputtered cells typically requires a low temperature diffusion to drive sufficient Cu into the CdTe to achieve a heavily doped layer at the CdTe/metal interface. However, if the diffusion is too deep, it can cause deterioration of the CdS/CdTe interface and decreased cell performance. The ability to control the Cu diffusion seems to be very important for successful back contact fabrication in CdTe solar cells. We showed in Ref. [14] that reducing the amount of Cu and diffusion time could lead to improved cell performance. Cells with our standard $2.3\ \mu\text{m}$ of CdTe typically require $40\ \text{\AA}$ of Cu under $100\text{--}200\ \text{\AA}$ of Au and diffusion at 150°C for 45 min.

Fig. 3 shows the I - V plots of the best cells prepared with various CdTe thicknesses while holding constant the conditions of the CdCl_2 treatment (10 min) and the Cu diffusion (18 min). For comparison, we have included an I - V plot of one of the best cells achieved in our lab [13]. This cell had a standard 30 min CdCl_2 treatment and 45 min back-contact diffusion. Compared with our laboratory best cell with $2.3\ \mu\text{m}$ of CdTe, the best cells with 1.28 and $0.87\ \mu\text{m}$ of CdTe, exhibit some roll-over in the forward current quadrant at currents above twice the light-generated current or above $\sim 40\ \text{mA}/\text{cm}^2$. The thinnest cell,

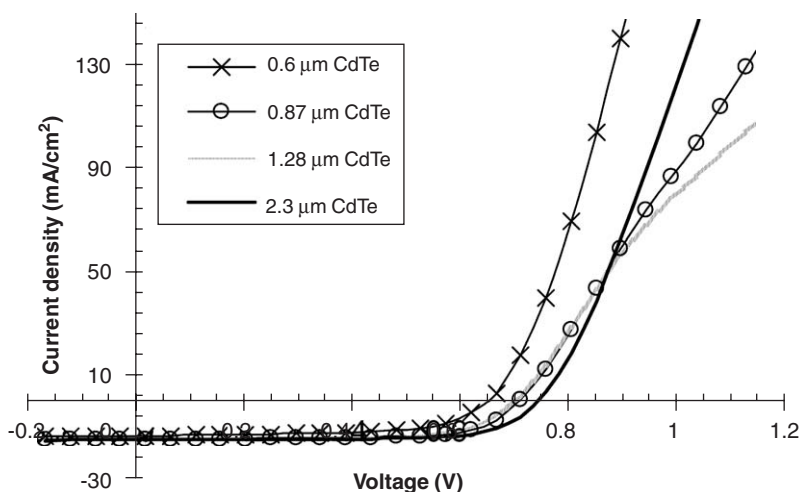


Fig. 3. I - V curves for cells prepared with 0.6 , 0.87 , 1.28 and $2.3\ \mu\text{m}$ thick CdTe.

with 0.6 of CdTe, did not show this rollover but had a substantially reduced V_{OC} of 710 mV. These characteristics will be discussed further below.

Table 1 shows the dependence of CdS thickness as well as the effect of CdCl₂ treatment and back-contact diffusion duration on the I – V performance of these cells. The rows are grouped according to common CdS thickness with our standard 2.3 μ m CdTe structure given in the first row. Note that with a constant 0.13 μ m CdS layer the thickness of the CdTe layer can be reduced to 0.87 μ m with only a minor loss of efficiency from 13% to 11.8%. However, the best results with 0.87 μ m of CdTe require reducing the CdCl₂ process time to 10 min at 397 °C and reducing the copper layer thickness from 30 to 15 Å while reducing the back contact diffusion time to 18 min at 150 °C in air. To illustrate the effect of the copper, Cell 184A2 was processed with no Cu and no diffusion but did receive the usual 200 Å gold dot which normally covers the copper. This cell exhibited a much lower V_{OC} and FF and yielded only 8.1% efficiency. Two cells are shown with CdS reduced to 0.08 μ m and CdTe reduced to 0.6 μ m (190A1 and 190B1). With this combination of thin CdS and CdTe layers, again there is a considerable improvement in the cell (190B1) that was processed with a shorter CdCl₂ treatment and with less Cu and less diffusion. Finally, the best cell having the thinnest CdS (0.05 μ m) and also ultra-thin CdTe (0.7 μ m) yielded good performance, again if the chloride process time was reduced to 10 min, the Cu thickness reduced to 15 Å, and diffusion reduced to 10 min.

Table 1 shows clearly that while the J_{SC} of the cells remained almost the same, the V_{OC} decreased as CdTe thickness decreased. The fill factor (FF) of the cells, which often depends strongly on the back-contact processing, did not have much variation for various diffusion times. The worst FF was obtained for ultra-thin cells diffused for longer duration (in Table 1, sample 190A1) pointing toward excess Cu out-diffusion from the back contact into the junction region. The V_{OC} of the cell also increased with the decrease in diffusion

Table 1
Effect of processing conditions on best cell performance

Sample ID	CdS (μ m)	CdTe (μ m)	CdCl ₂ (min)	Back contact (Cu)	Back-contact diffusion (min)	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF (%)	η (%)
980A2	0.13	2.3	30	30 Å	45	807	22.3	72.3	13.0
184A1	0.13	1.28	30	30 Å	30	714	21.3	65.9	10.0
184B1	0.13	1.28	10	30 Å	30	710	22.3	61.4	9.7
184B2	0.13	1.28	10	15 Å	18	767	22.1	66.8	11.3
188A1	0.13	1.04	10	15 Å	18	795	21.2	70.8	11.9
184A2*	0.13	1.04	30	0	No diffusion	641	20.9	60.4	8.1
189A1	0.13	0.87	10	15 Å	18	772	22.0	69.7	11.8
190A1	0.08	0.6	30	30 Å	30	484	20.1	44.0	4.3
190B1	0.08	0.6	10	15 Å	18	708	20.5	64.6	9.4
187A1	0.07	0.94	10	15 Å	10	762	22.6	67.4	11.6
225A1	0.05	0.7	10	15 Å	10	750	21.7	69.2	11.2

980A2—Standard 2.3 μ m cell with standard processing [13].

184A2*—No Cu, only Au back contact.

The bold values signify high efficiency cells.

duration. Efficiencies of more than 11% were obtained for all thicknesses of CdTe from 0.7 to 1.28 μm .

We find that the CdS thickness did not have much effect on efficiency as it is reduced from 0.13 to 0.05 μm along with CdTe thickness. The J_{SC} is expected to increase with reduction in CdS thickness due to more transparency for higher energy photons, but reduction in CdTe thickness decreases J_{SC} due to less absorption of red photons. Secondly, thinner CdS also reduces open-circuit voltage. The post deposition processing of 10 min CdCl_2 treatment, 15 Å Cu in back contact and 10 min of back contact diffusion was found optimum for cells with less than 1 μm thick CdTe.

Although the best thin CdTe cell was obtained with $\sim 1 \mu\text{m}$ CdTe and had efficiency of 11.9%, cells with 0.7 μm CdTe showed efficiency that was only slightly less, 11.2%. *To our knowledge, this is the thinnest CdTe cell ever reported with efficiency above 10%.* These efficiencies are only ~ 10 –15% (relative) lower from the best cell (13%) we have made on commercial soda-lime TCO-coated glass (TEC-7) obtained with our standard CdTe (2.3 μm) layer, with longer CdCl_2 treatment (30 min) and longer back-contact diffusion (45 min) time [13]. The lower efficiencies are due to loss in V_{OC} not in J_{SC} .

Fig. 4 shows the QE of the ultra-thin CdTe cells as described in the I – V discussion above. The QE of the cells decreases in the longer wavelengths but only marginally, as CdTe thickness decreases, due to un-collected photons from this region. The QE of ultra-thin CdTe cells with this improved post-deposition processing are higher than the QE of cells (Fig. 5) with standard post deposition treatment but showed similar shape. When CdTe thickness becomes extremely thin ($\sim 0.6 \mu\text{m}$ CdTe), the QE with improved processing is much higher. The QE of the 0.6 μm cell is higher in the short wavelength region due to the thinner CdS (0.05 μm) giving higher transmission in the blue.

One aspect of the cells with ultra-thin CdTe, however, was significantly poorer V_{OC} than our standard processed cells. The yield (fraction of cells on the same plate that performed within 90% of the maximum) of good cells on the 0.7 μm CdTe plate was low ($\sim 20\%$).

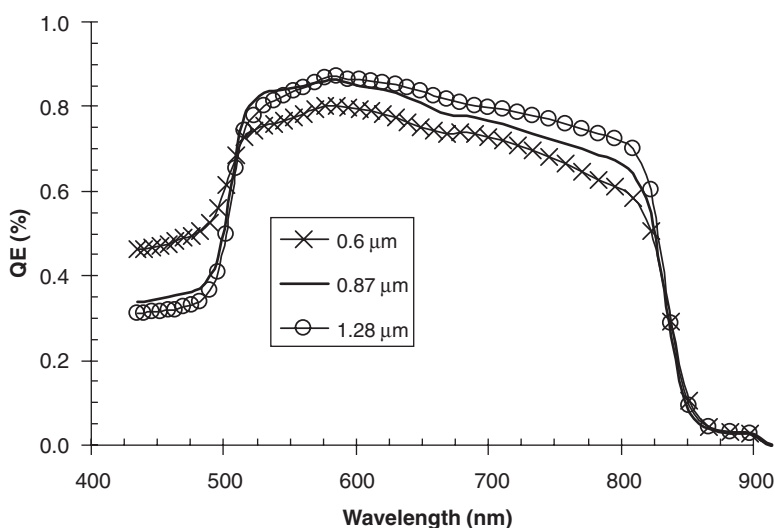


Fig. 4. QE plots for cells prepared with improved processing.

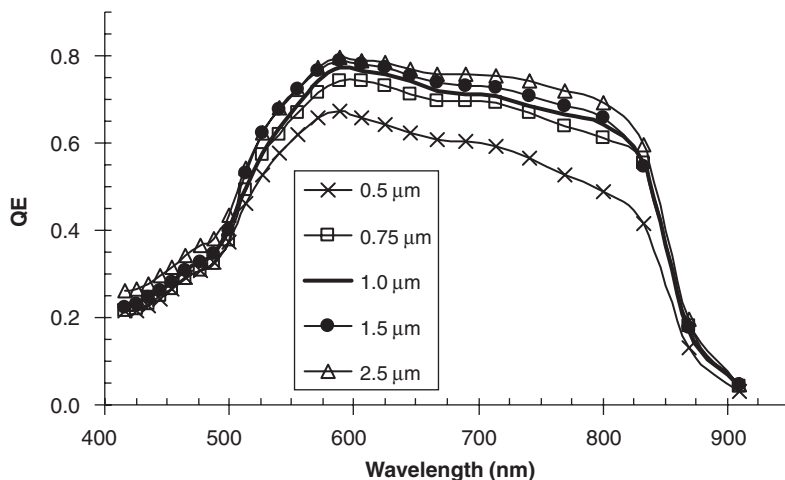


Fig. 5. QE plots of cells prepared with standard post deposition processing.

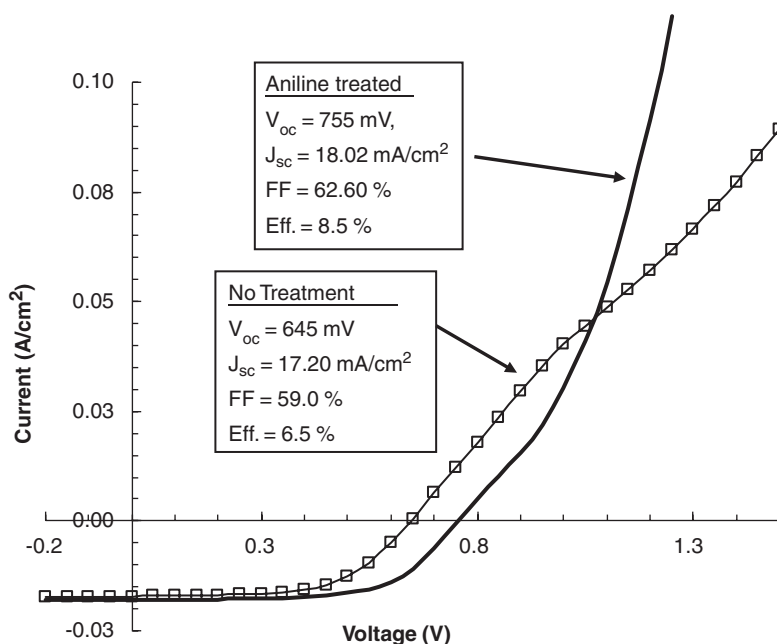


Fig. 6. I - V of ultra-thin CdTe cell with and without aniline treatment.

Low V_{OC} and yield could be due to shunting because of weak diodes and non-uniformity [15]. In order to increase the yield, we used an improvement technique which was recently published from our group [16]. To test the suitability of this yield improvement process on these ultra-thin CdTe cells, we purposely selected a plate with $\sim 1 \mu\text{m}$ thick CdTe which showed lower average efficiency of 6.1%. A piece of this plate was treated in aniline [16]

and then processed together with an untreated sister piece for back contacting and diffusion. While the aniline treatment increased the V_{OC} and FF from an average of 642 mV and 55.8% to 755 mV and 61.1%, there was almost no change in J_{SC} . The average efficiency increased from 6.1% to 8% after the aniline treatment. This improvement of >30% is due to a decrease in shunting which shows up in an increase in V_{OC} and FF. Fig. 6 shows the effect of aniline treatment. The higher slope in the I – V plot of the aniline treated sample confirms the formation of a better back contact. This also suggests that ultra-thin CdTe cells (below 1 μ m) may have a higher density of weak diodes and probably more non-uniformity. Further optimization of aniline treatments and other approaches (e.g., the use of a high resistivity SnO_2 layer between the conducting $SnO_2:F$ and CdS) to reduce the effect of weak diodes and non-uniformity is in progress.

4. Conclusion

We are able to reduce the CdTe thickness from 2.3 to 0.7 μ m in CdS/CdTe solar cells without losing much efficiency. Optimization of post-deposition $CdCl_2$ treatment and back-contact diffusion conditions led to the achievement of an 11.8% efficient cell with $\sim 0.87 \mu$ m CdTe which is only a 9% relative loss from that of our standard 2.3 μ m CdTe 13% cell. We also achieved 11.2% efficiency using only 0.05 μ m CdS and 0.7 μ m CdTe which to our knowledge is the thinnest reported CdTe cell with high efficiency. Although we achieved quite a high efficiency from ultra-thin CdTe cell, the yield is poor. The aniline treatment of weak diodes and shunts significantly improved the performance of the cells.

Acknowledgements

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