Co-sublimation of $\text{CdSe}_x\text{Te}_{1-x}$ layers for CdTe Solar Cells

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Abstract

CdTe thin film solar cells have demonstrated efficiencies over 20%, but CdTe has a somewhat higher band gap than optimal for single-junction terrestrial solar-cell power generation. A reduction in the band gap could therefore result in an overall improvement in performance. To reduce the band gap, selenium was alloyed with CdTe using a novel co-sublimation extension of the close-space-sublimation process. Co-sublimated layers of CdSeTe with various selenium concentrations were characterized for optical absorption and atomic concentrations, as well as to track changes in their morphology and crystallinity. The lower band-gap CdSeTe films were then incorporated into the front of CdTe cells. This two-layer band-gap structure demonstrated higher current collection and increased quantum efficiency at longer wavelengths.

Keywords: CdTe; Thin Film Photovoltaics; CdSeTe; Physical Vapor Deposition

1. Introduction

The growing photovoltaic (PV) market requires technologies that utilize economic large-scale manufacturing with high device efficiency. Cadmium-telluride (CdTe) has been expanding in the PV market because of its proven low cost manufacturing and a band gap that is near optimum. First Solar using the CdTe technology has demonstrated PV generated energy cost at 0.0387 \$/kWhr and have developed small-area CdTe cells with efficiencies up to 21.5% [1, 2].

Geisthardt et al., further characterized the potential of the CdTe technology with an analysis of performance limits under various real world conditions theorizing fundamental limits of the technology [3]. This model projected that if the CdTe band gap were reduced from 1.5 eV to 1.38 eV, the increase in current would more than compensate for the voltage and fill-factor reductions and result in a net increase in efficiency.

A reduction in the CdTe band gap has been demonstrated through selenium alloying [4, 5], reducing the band gap of CdTe to 1.39 eV [6]. Paudel and Yan showed that by sputtering CdSe between the front contact and CdTe layers a cadmium selenium telluride (CdSeTe) layer was formed during the CdCl_2 process [7]. The addition of this CdSeTe layer resulted in improved current collection at long wavelengths. The sputtered CdSe technique was dependent on diffusion of selenium from the CdSe sputtered layer. Since CdSe likely causes poor cell performance in this structure, the sputtered CdSe layer must be fully defused into CdTe forming CdSeTe. Thus the sputtered CdSe layer acted as a selenium reservoir while the CdCl_2 passivation drove the diffusion of selenium into the CdTe layer. This method makes more complicated band gap gradings or the formation of uniform single band gaps below 1.5 eV difficult.

This paper will study the material and electrical properties of as-deposited CdSeTe alloys, demonstrating control over the selenium alloying. As-deposited single band-gap CdSeTe alloys will be used for characterization to assess material changes as the selenium incorporation is increased. Finally the single band gap CdSeTe layer will be deposited at the front of a CdTe cell to assess increased current collection at longer wavelengths similar to the sputtered CdSe method [7].

2. Co-Sublimation Hardware and Characterization

Co-sublimation technology has been developed at Colorado State University to allow CdTe to be alloyed with magnesium [8]. This technology has now been further developed to incorporate selenium in place of magnesium to allow for the controllable deposition of CdSeTe. This enhanced hardware (See Fig. 1) includes additional transfer holes around the perimeter of the CdTe source to improve band gap uniformity across the film. Due to the increased vapor pressure of selenium [9] active water cooling was added to the selenium bottom source to maintain a reduced operating temperature. To allow the selenium flux to be quickly turned on or off, a shutter was added above the selenium source. All CdSeTe films were deposited on Pilkington Tec10 substrates with a magnesium zinc oxide (MZO) buffer layer [9, 10]. This 100-nm buffer layer was RF-sputtered onto the substrate at room temperature with a magnesium composition of $x=0.25$ in the film. The MZO was used in place of CdS for increased current collection and improved band alignment in CdTe cells [10]. These substrates with the 100-nm MZO buffer layers were used for all characterization films and device.

Optical properties of the CdSeTe films were analyzed with a Mikropack DH-2000-BAL UV-VIS-NIR light source and an Ocean Optics USB4000-VIS-NIR spectrometer. Band gaps were calculated using the Tauc plot method, where $(\alpha h\nu)^2$ was plotted against photon energy, $h\nu$, and the linear portion of $(\alpha h\nu)^2$ was extrapolated to where $\alpha=0 \text{ cm}^{-1}$ (i.e., the x-axis). A JOEL

JSM-6500F field emission scanning electron microscope (SEM) and a Nanoscience atomic-force microscope (AFM) were used for morphology and imaging. Film composition was derived from energy dispersive x-ray spectroscopy (EDS) and a PE-5800 x-ray photoelectron spectroscopy (XPS). XPS samples received a 120 second, 5kV sputter cleaning treatment to remove carbon and oxide peaks typical of surface contamination. Glancing angle x-ray diffraction (GAXRD) was performed at an incidence of 1.5° with a Bruker D-8 Discover utilizing Cu K_α radiation ($\lambda=1.542 \text{ \AA}$). Standard current-voltage and quantum efficiency facilities were used for cell-performance and characterization

Fig. 1. Co-sublimation hardware for alloying CdTe and selenium. The selenium vapor pressure is directed into the CdTe pocket to allow sublimation of the alloy.

3. CdSeTe Films

3.1. Composition

The co-sublimation source in Fig. 1 allows the band gap of the CdSeTe film to be controlled through the amount of selenium flux from the bottom source by controlling its temperature. Fig. 2a shows a set of transmission curves for $\sim 1.0 \mu\text{m}$ thick CdSeTe films deposited at various selenium source temperatures. As the selenium source temperature is increased, the transmission curves shift to the right, which indicates a decrease in band gap by as much as 80 meV. Tauc-plot analysis was conducted on these curves over a selenium-source temperature range from 180 °C to 227.5 °C. Fig. 2b gives the resulting band gap vs. selenium source temperature, demonstrating the controllability of the co-sublimation hardware for CdSeTe deposition. The band gaps deduced from the transmission curves decreased CdTe at 1.5 eV to approximately 1.4 eV, then rose sharply towards the CdSe band gap at 1.7 eV. This change in band gap with increasing Se concentration is consistent with previous CdSeTe materials reported in the literature [6].

Fig. 2. a) Optical transmission of CdSeTe films at various selenium bottom source temperatures b) Tauc-plot-calculated band gaps vs. selenium source temperatures. As the selenium source temperature is increased, the selenium vapor flux is increased and the CdSeTe band gap first decreases, then rises sharply.

The reduction in band gap of CdSeTe compared to 1.5 eV CdTe or 1.7 eV CdSe is due to band gap-bowing [4]. X-ray photoelectron spectroscopy (XPS) and electron-diffraction spectroscopy (EDS) were performed for elemental analysis, which allowed the cadmium, tellurium and selenium atomic concentrations to be determined. Fig. 3a shows the XPS atomic concentrations for Cd, Te, and Se at various selenium bottom source temperatures. The 3d₅ peak was used to approximate the atomic concentration for Cd and Te, and the 3d peak for selenium. Fig. 3b shows the atomic concentrations measured by EDS, which are consistent with the XPS measurements.

Fig. 3. Atomic concentrations of Cd, Te, and Se as measured by a) XPS and b) EDS show increased selenium incorporation at higher temperatures.

Fig. 4 combines the band gaps calculated from the absorption curves with the selenium concentrations determined from XPS and EDS. The minimum band gap observed was 1.41 eV at a selenium concentration of $x = 0.35$ as measured by EDS and $x = 0.45$ as measured by XPS. These values are consistent with those from hot-wall-deposited and MBE-grown CdSeTe films [5, 6]. The EDS values are believed to be a better representation of the bulk properties, since XPS is more sensitive to surface contamination and subjective to preferential sputtering. The EDS data, which utilized a 15 kV electron excitation beam, should therefore be close to the bulk characterization, and further analysis below will use the EDS concentrations. Note that the CdSeTe concentrations become highly sensitive to source temperatures above 220 °C.

Fig. 4: CdSeTe band gap as a function of selenium concentration as measured by XPS and EDS.

3.2. Morphology

The surface morphology of the CdSeTe film changes as the selenium concentration is increased. Fig. 5 shows scanning electron microscope images of the CdSeTe deposited film with varying selenium concentrations. At $x = 0.14$ the grains become more faceted and tightly packed, and as x is increased to 0.36, the faceted nature of the grains remains with a minor reduction in grain size. Note $x = 0.36$ should be approaching the optimal band gap for a single junction solar cell. As the selenium concentration is increased to $x=0.66$ the grains appear to further reduce in size and begin losing the faceted feature. AFM measurements show similar morphology changes to SEM with an increase in the RMS roughness from $x = 0.4$ to 1.0 as presented in Table 1.

Fig. 5. SEM images at $x = 0.01, 0.14, 0.36$, and 0.66 . A clear change in morphology is seen as the selenium concentration is increased. Se concentration x is estimated from EDS.

Table 1
RMS Roughness vs Selenium concentration (x)

$Se(x)$	$0.01 - 0.37$	0.54	0.72	0.95	0.97
RMS (nm)	38 - 43	51	62	102	125

3.3. Crystallinity

Fig. 6 gives glancing angle XRD of films with a varying selenium concentrations over the full range from $x = 0$ to 1. Key peaks are identified, and it is seen that the dominant orientation of the CdTe grown on MZO is 111 with very small peaks at 220 and 311. Fig. 7 shows an expanded view of the 111 peak as a function of selenium concentration. As the selenium alloying is increased from $x = 0$ to 0.35, the 111 peak shifts to the right, indicative of band bowing as the lattice constant for the CdSeTe material moves towards the CdSe zinc-blende limit. At x near 0.6, however, the material shifts structure from cubic zinc-blende to hexagonal wurtzite [10]. This is identified by the development of the peak at $2\theta = 45.6^\circ$, which corresponds to the CdSe 103 peak. The 111 peak intensity decreases up to $x = 0.35$, and when the material becomes hexagonal, the CdTe 111 peak is replaced by a CdSe 002 peak near the previous CdTe 111 location. The CdSe 103 peak then increases in intensity as the material approaches CdSe. At $x = 0.35$, the material has the lowest band gap seen in this study, and the CdSe 103 and 112 peaks have begun to appear suggesting that the structural phase transition is under way. Theoretically a band gap of 1.38 eV is desired [3], but mixing of CdTe cubic zinc-blende and CdSeTe hexagonal wurtzite interface may limit the band-gap decrease.

Fig. 6. Glancing Angle (1.5°) XRD at varying selenium concentrations, showing the shift from a cubic to hexagonal structure.

Fig. 7. 111 XRD peak with varying selenium concentration. The 111 peak shifts to the right as the selenium concentration is increased, then disappears at the structural transition.

The lattice constant a_0 for the cubic structure is calculated using equation 1 and lattice constants a_0 and c_0 for the hexagonal structure using equation 2. The lattice constants are calculated using the miller indices (hkl), peak location θ , and the wavelength of the incident x-ray beam ($\lambda_{K\alpha 1, Cu} = 1.5405 \text{ \AA}$). Fig. 8 gives the calculated lattice constant of CdSeTe films from $x = 0$ to 0.35 , where the film is believed to be cubic. The lattice constant decreases from CdTe at $6.48 \text{ \AA}$ (zinc-blende) towards CdSe at $6.08 \text{ \AA}$ (zinc-blende) until the film becomes hexagonal [11, 12]. Table 2 gives the calculated lattice constants above $x = 0.60$ with literature values for hexagonal CdSe.

$$\sin^2(\theta) = \frac{\lambda^2}{4a_0^2} (h^2 + k^2 + l^2) \quad (1)$$

$$\sin^2(\theta) = \frac{\lambda^2}{4} \left(\frac{4}{3} \left(\frac{h^2 + hk + k^2}{a_0^2} \right) + \frac{l^2}{c_0^2} \right) \quad (2)$$

Fig. 8. Lattice constant (a_0) calculated from XRD as a function of selenium concentration (x) with CdTe (Zinc-Blende) and CdSe (Zinc-Blende) referenced [13]

Table 2
XRD lattice constants calculated after material shifts to wurtzite, *literature given values [13].

x	2θ (deg)	$d(103)$	a_0	$d(002)$	c_0
0.66	24.8	2.021	4.385	3.581	7.162
0.94	25.3	1.983	4.305	3.512	7.023
0.96	25.4	1.981	4.301	3.509	7.018
1.0*	-	-	4.300	-	7.010

4. Cell Performance

4.1. A CdSeTe/CdTe Device Fabrication

The co-sublimated hardware has demonstrated an ability to deposit CdSeTe films at various band gaps with a high level of control. To demonstrate increased current collection at higher wavelengths, these lower band gap CdSeTe films were incorporated between the Tec10/MZO and CdTe layers, similar to the sputter CdSe process [7]. The CdSeTe/CdTe cells were then processed using CSU's standard techniques [9]. No re-optimization of the process conditions, including the Cl passivation, was performed. Fig. 9 shows the CdSeTe/CdTe cell structure that was fabricated. The baseline CdTe solar cell was deposited at CSU using its standard inline close-space-sublimation technology [9]. In this research, a MZO front contact was used instead of the traditional CdS layer to improve the current collection and a tellurium back contact is used in place of carbon paint [9, 10, 14]. The tellurium back contact was evaporated at 10^{-5} Torr at 1 nm/s. CdSeTe layers were co-sublimated at 10 nm/s onto the Tec 10/MZO substrate at a temperature of 470 °C in a 40 mTorr argon environment. The thickness of the CdSeTe layer was varied from 0 to 400 nm for each of the three discrete band gaps: 1.47, 1.45, and 1.41 eV. The MZO/CdSeTe film was then re-inserted in the primary chamber, where it was heated to 470 °C and the CdTe, CdCl₂ and copper doping steps were completed [9]. The absorber thickness was maintained at 2.2 μ m.

TEC 10 Glass / TCO (3 mm)
Magnesium _{0.25} Zinc _{0.75} Oxide (100 nm)
Cadmium Selenide _x Telluride _{1-x} (0-400 nm)
Cadmium Telluride (1.8 μ m – 2.2 μ m)
Copper Doped Cadmium Telluride (0.2 μ m)
Tellurium (50 nm)
Nickel Paint (50 μ m)

Fig. 9. CdSeTe/CdTe structure to assess the CdSeTe ability to collect photons below 820 nm.

4.2. CdSeTe/CdTe Cell Performance

Fig. 10 shows the average J-V performance parameters and their standard deviations for cells with three CdSeTe band gaps: 1.47, 1.45, and 1.41 eV at various thicknesses in each case from 0 (a reference cell of CdTe without any CdSeTe layer) to 400 nm. The standard deviation is calculated over the 25 devices measured per substrate. Fig. 11 shows representative J-V curves for 1.47, 1.45, and 1.41 eV CdSeTe/CdTe devices with a 200-nm thick CdSeTe layer.

There is a V_{oc} reduction for all band gaps of CdSeTe compared to absorbers with CdTe only, as expected when the front-junction band gap is reduced [3]. The V_{oc} was slightly larger at 1.45 eV (810 mV) compared to 1.47 eV (795 mV) or 1.41 eV (750 mV), probably due to a process factor that was not identified. All three band gaps show a consistent increase in performance as the CdSeTe thickness is increased from 25 to 200 nm. This may be associated with different process optimizations for each set point including $CdCl_2$ passivation and copper doping.

The MZO band alignment can be turned by changing the magnesium content in the MZO film [10]. The CdSeTe layer likely has a slightly different band alignment compared to CdTe and may require a new optimization of the magnesium content in the MZO for a MZO/CdSeTe interface [10]. The lattice mismatch between layers may also be affecting the overall performance. The CdSeTe layer could act as a buffer between the lattice mismatched MZO/CdTe interface. The fill-factor (FF) shows a similar trend to V_{oc} , and reaches values similar to the reference cells when it is at 200 nm and 1.45 eV.

The short circuit current shows an increase from 24.5 to 26.0 mA/cm^2 as CdSeTe thickness increases from 0 to 400 nm at 1.45 eV and similarly for 1.47 eV. This is consistent with an increased absorption of the reduced band-gap CdSeTe layer and is evidence that the collection efficiency of the CdSeTe is reasonably good. The cells with 1.41 eV CdSeTe began to show comparable current collection (24.0 mA/cm^2) at 100 nm, but decreased dramatically (to 15.4 mA/cm^2) at 400 nm.

Fig. 10. JV performance parameters of MZO/CdSeTe/CdTe devices with the CdSeTe layer at 1.47, 1.45, and 1.41 eV. The CdSeTe thickness is swept from 0 – 400 nm. Average device values are used with a plus/minus one standard deviation error bar. J_{sc} at 1.41 eV and 400 nm is 15.4 mA/cm^2 .

Fig. 11. JV of 1.47, 1.45, and 1.41 eV CdSeTe/CdTe cells at 200 nm CdSeTe thicknesses.

The 1.41 eV CdSeTe cells showed inferior performance to the others with reductions in V_{oc} , FF and J_{sc} . This may be because as the CdSeTe material approaches 1.41 eV, the film is starting to transition from the cubic zinc-blende structure to the hexagonal wurtzite structure as shown by XRD, which is likely not ideal for an interface with the cubic zinc-blende CdTe. Increased CdTe/CdSeTe interface recombination may potentially reduce the performance at 1.41 eV as the materials crystallinity changes. Maintaining a cubic structure as the CdSeTe band gap is minimized may prove critical for maintaining performance improvement.

Fig. 12 shows the quantum efficiency (QE) of the cells with 1.45-eV band-gap CdSeTe layers at various thicknesses from 0 to 400 nm. As the CdSeTe layer thickness is increased, a shift in the absorbed band edge can be seen at ~850 nm. The increased absorption of the CdSeTe layers at lower wavelengths is indicative of a lower absorber material. The integrity of the lower band-gap CdSeTe was maintained through the passivation process and it clearly contributes to current collection. The QE derived band gaps are calculated by taking the max negative derivative of the QE curves [15]. The QE derived band gaps are tabulated in table 3 with the band gaps from optical absorption as reference. The Tauc plot measurements and derived QE band gaps give similar values. Tauc plots are measured prior to CdTe deposition and $CdCl_2$ passivation while QE derived band gaps are measured on completed devices. The agreement between the two implies that the reduced band gap of the CdSeTe layers is maintained. Selenium diffusion remains to be characterized between layers.

Fig. 12. QE of 1.45eV CdSeTe/CdTe cells at various CdSeTe thicknesses. Greater photon collection above 840 nm is seen with increasing CdSeTe thickness.

Table 3

Calculated band gaps (eV) of the minimum bulk absorber from integrating the QE at various CdSeTe thickness (nm) [15]. The measured tauc plot band gaps are listed for reference and the max J_{sc} measured from JV and QE integration.

		QE Derived Band Gaps (eV)						J_{sc} (mA/cm ²)		
		CdSeTe Thickness (nm)						QE	JV	JV
Se (x)	0 nm	25 nm	50 nm	100 nm	200 nm	400 nm	Tauc	200 nm	0 nm	
0.025	1.51	1.51	1.51	1.51	1.50	1.47	1.47	25.0	25.5	24.3
0.045	1.51	1.50	1.50	1.50	1.48	1.46	1.45	25.7	26.0	24.5
0.166	1.51	1.49	1.49	1.49	1.43	1.41	1.41	23.4	23.3	23.9

5. Conclusion

Since a reduction in the CdTe band gap from 1.5 to 1.38 eV should result in increased cell current and performance, a new co-sublimation deposition source was developed to manufacture selenium-alloyed CdTe films. Controllable alloying of CdSeTe films was demonstrated and achieved a minimum band gap of 1.41 eV with notable changes to morphology and crystallinity with increasing selenium concentration. Various thickness and selenium concentrations of CdSeTe films were deposited at the front of CdTe solar cells. The lower band-gap CdSeTe/CdTe cells showed a shift in the QE cutoff to longer wavelengths, consistent with measured transmissions curves and demonstrated larger currents with thicker alloy layers.

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