

# $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ thin films and junctions

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## Abstract

Cadmium zinc telluride has a tunable band gap in the 1.45–2.26 eV range and is therefore a suitable candidate for the top cell in tandem solar cell applications. The aim of this work is to investigate the potential of polycrystalline thin films of  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  for solar cell applications. Two deposition technologies, cosputtering and co-close-spaced sublimation (co-CSS) were used for the deposition of  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ . Both processes were calibrated to yield a band gap of 1.65–1.75 eV, the optimum range for tandem solar cells. Single-phase  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  films have been obtained with both technologies. Films deposited by cosublimation exhibited larger grain size and overall better microstructure than films deposited by sputtering.  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ -based junctions of the superstrate configuration have been fabricated. Various wide band gap materials, such as CdS,  $\text{SnO}_2$ , ZnO, and ZnSe were utilized as window layers. Solar cell performance for as-deposited junctions was found to be limited due to poor collection. Improvements in collection and overall solar cell characteristics can be attained by subjecting the devices to a postdeposition heat treatment. Although junctions based on CdS yielded the highest  $V_{OC}$ 's, the most improved collection and highest  $J_{SC}$ 's were demonstrated with CZT/ $\text{SnO}_2$  junctions.

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## 1. Introduction

Single junction thin film solar cell efficiencies have exceeded the 15% efficiency mark and are steadily progressing toward 20% clearly demonstrating the potential of these technologies. At the module level, performance has been equally impressive with over 10% efficiencies being reported. As thin film technologies continue to mature and play a significant role at the market place, it becomes necessary to begin the process of identifying next generation devices and materials with the potential of yet higher power output. A natural extension to today's thin film technologies with the potential of achieving higher efficiencies are thin film-based tandem solar cells. A combination of a top and bottom cells with band gaps of 1.6–1.8 and 1.0 eV, respectively, has been shown to have the potential for practical efficiencies of 25% [1]. Copper indium gallium

diselenide (CIGS), the most efficient thin film solar cell, has a band gap of 1.0 eV, making it the first choice for the bottom cell, leaving the top cell device (with a 1.7 eV absorber) as the first major issue to be addressed in the development of tandem thin film solar cells. Cadmium selenide (CdSe) has a band gap of 1.7 eV, and its potential for this application has been demonstrated [2]. Cadmium zinc telluride ( $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  or CZT), a ternary II–VI compound semiconductor with a tunable band gap between 1.45 and 2.25 eV, is also a potential candidate. This material could also benefit from the existing knowledge base associated with CdTe devices. This paper reviews results from a study to develop CZT-based junctions for use in tandem thin film solar cells.

## 2. Experimental

For this work, thin films of CZT were deposited by two deposition technologies: rf cosputtering of ZnTe and CdTe targets (both of 99.999% purity), and co-close-spaced

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sublimation (co-CSS) of ZnTe and CdTe powders (of 99.99% purity). The two methods were chosen in order to be able to study CZT-based junctions over a wide range of deposition temperatures (250–600 °C); the substrate temperature is one of the important processing parameters for CdTe solar cells [3]. For both technologies, the deposition conditions were adjusted in order to obtain the composition necessary for a band gap in the range of 1.65–1.75 eV. The composition of sputtered-deposited films could be easily controlled by controlling the deposition rate of CdTe and ZnTe through the power applied to the two 3" sputtering sources; the power density for ZnTe and CdTe was in the range of 17–20 and 11–13 W/in<sup>2</sup>, respectively. The substrate temperature for sputtered CZT films was in the range of 250–350 °C, and Ar or an Ar/N<sub>2</sub> mixture was used as the sputtering ambient. Spatial uniformity of the films was achieved by employing substrate rotation and positioning the sputtering sources at an angle of approximately 22.5° with the normal to the substrate; the deposition area was approximately 6×6 cm<sup>2</sup>. Achieving the desired composition and spatial uniformity for co-CSS-deposited films was not as trivial. The co-CSS deposition system is similar to that described previously for the deposition of CdTe films [3]. For the deposition of CZT films, both source materials, ZnTe and CdTe, were placed onto the same graphite plate and were therefore heated to the same sublimation temperature. The relative amounts of the two materials were adjusted to account for differences in their dissociation temperatures and sticking coefficients, until the desired film composition was obtained. The process was optimized for a specific range of deposition parameters; for a source–

substrate spacing of 4 mm, source and substrate temperatures in the range of 630–660 and 500–580 °C, respectively, and a stationary He ambient (1–5 Torr), a CdTe to ZnTe ratio of approximately 1:10 yielded films with a band gap in the 1.65–1.75 eV range; the deposition area for the CSS process was approximately 3×3 cm<sup>2</sup>, significantly smaller than the sputtering process. Junctions and solar cells were fabricated in a superstrate configuration typical of CdTe devices, i.e., glass/TC/window layer/CZT/back contact. Several window materials were used including CdS, SnO<sub>2</sub>, ZnO, and ZnSe; back contacts to CZT were formed using approaches that have been effective for CdTe solar cells; these included doped graphite paste and ZnTe/Cu. CZT films were characterized using optical transmission, XRD, SEM, EDS, and AES measurements; solar cells were evaluated using standard *J–V* and spectral response measurements.

### 3. Results and discussion

#### 3.1. Thin films

Results presented in this section are for as-deposited films, although for solar cell fabrication, postdeposition heat treatments were also employed. Thin film characterization focused on two issues: (a) provide a comparison of the quality of CZT films prepared by sputtering and CSS, and (b) demonstrate uniformity and composition control over the deposition areas, since this material is a ternary and is being deposited from the constituent binaries by codeposition methods. Fig. 1 compares SEM images of CZT films

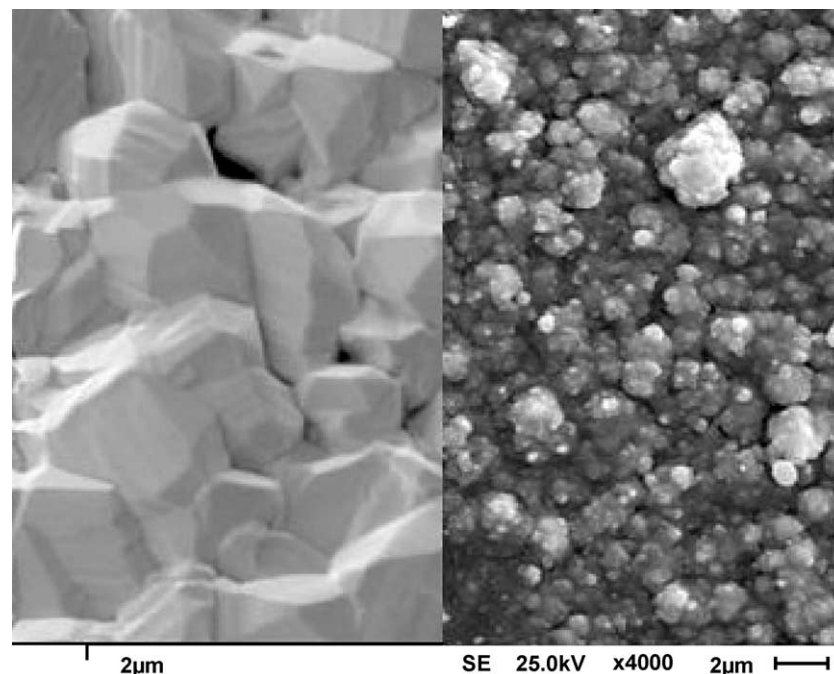


Fig. 1. SEM micrographs of CSS- (left) and sputter-deposited (right) CZT films of similar compositions.

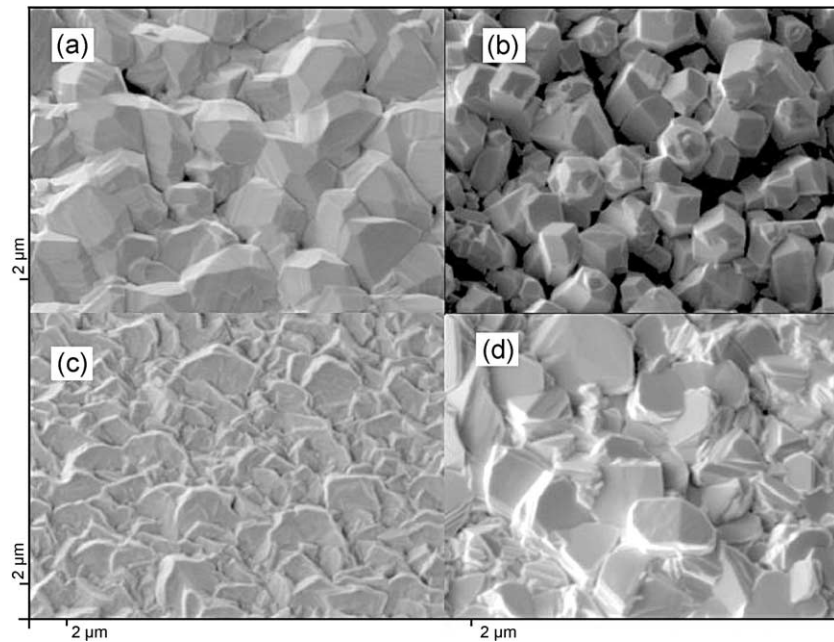


Fig. 2. SEM micrographs of CZT films deposited by CSS on (a)  $\text{SnO}_2$ , (b)  $\text{CdS}$ , (c)  $\text{ZnSe}$ , and (d)  $\text{ZnO}$ .

deposited by rf sputtering and co-CSS at 300 and 560 °C, respectively; both films were deposited on  $\text{SnO}_2$ -coated glass substrates. It is apparent that the co-CSS-deposited films exhibit superior grain structure with faceted grains that range in size from approximately 2 to 4  $\mu\text{m}$  (film thickness 5–6  $\mu\text{m}$ ). The sputtered film consists of smaller grains that appear to be comprised of clusters of smaller particles (film thickness 4  $\mu\text{m}$ ). It is apparent that co-CSS process yields CZT films structurally superior to sputtering; the higher substrate temperature for CSS is most likely the key parameter that dominates the nucleation process and leads to the improved crystallinity. Another set of SEM images is shown in Fig. 2, where CZT films were deposited by the co-CSS process on several window layers; all films were deposited to a thickness of  $5.0 \pm 1.0 \mu\text{m}$ . These images demonstrate the influence of the substrate material on the structural properties of CZT. Although the variations in grain size can be considered relatively small, the most densely packed films are those deposited in  $\text{ZnSe}$  and  $\text{ZnO}$ , while the film deposited on  $\text{CdS}$  clearly shows large voids, which in many cases developed into pinholes visible to the naked eye; the presence of pinholes would be detrimental to solar cells, and therefore for device fabrication to be discussed below, CZT films were typically deposited to a thickness of at least 5–6  $\mu\text{m}$  to ensure complete coverage of the substrate. All films shown were deposited under the same conditions, although it should be noted that run to run variations in composition could be  $\pm 5\%$  (as determined from EDS and optical transmission measurements). The differences in the structure of the CZT films shown in Fig. 2 are believed to be related to substrate properties, such as grain size, orientation, and lattice constant. The optical band gap of

CZT was calculated from  $\alpha^2$  vs.  $E$  data ( $\alpha$  determined from with optical transmission measurements). An example of transmission data for sputter-deposited films is shown in Fig. 3, where the transmission was measured at three different locations over the deposition area; the calculated band gap for these was in the range of 1.710 to 1.735 eV. The transmission spectra for co-CSS deposited films were similar and in all cases within 5% of the data of Fig. 3. For tandem solar cell applications, it would be highly desirable that the transmission is as high as possible. The compositional uniformity of CZT films, in particular those deposited by the co-CSS process, was also investigated in the thickness direction, using Auger measurements. A

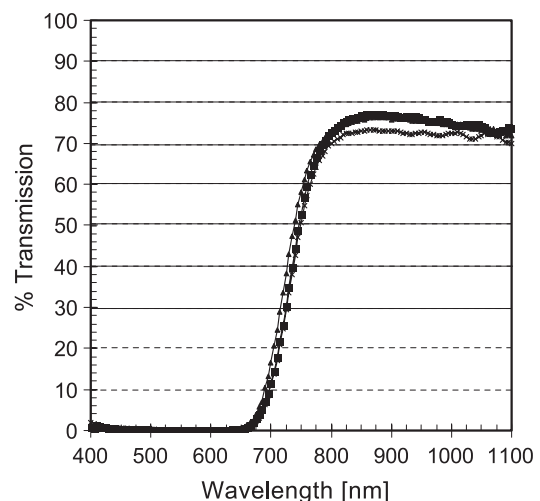


Fig. 3. Transmission spectra for CZT films deposited by cosputtering ( $E_G \approx 1.7 \text{ eV}$ ).

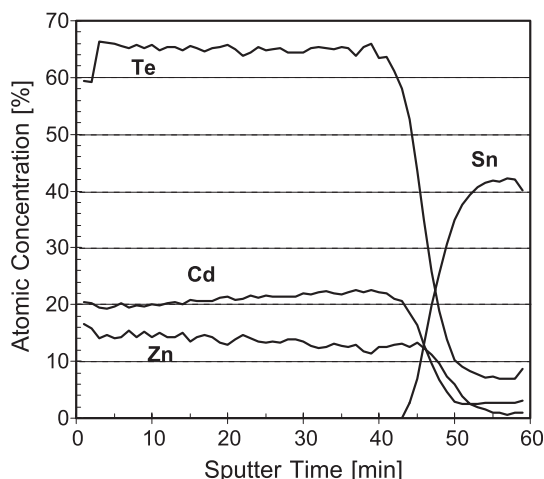


Fig. 4. Compositional depth profile for a CZT film deposited by CSS.

depth profile for a CZT/CdS/SnO<sub>2</sub>/glass structure is shown in Fig. 4 (only the elements Cd, Zn, Te, and Sn are shown for clarity). This particular sample shows a relatively small compositional variation (approximately 3%) with the amount of Zn increasing toward the surface of the CZT film (with Cd decreasing). Such a variation was observed in several CSS-deposited films (others exhibited a constant composition throughout the entire film thickness). It is believed that this behavior is associated with aging of the source, as CdTe was depleted faster than ZnTe. The presence of compositional gradients could lead to energy gradients within the CZT films that could aid or impede carrier collection. The band gap versus composition relationship for several CZT films was determined using EDS and XRD for composition, and  $\alpha^2$  vs.  $E$  for band gap calculations. All films characterized were found to be in very good agreement with previously published data; more details on these results can be found elsewhere [4]. The XRD measurements also indicated that CZT films deposited by both techniques were single-phase and did not contain CdTe or ZnTe. Films deposited by CSS were found to exhibit a higher degree of crystallinity as indicated by the intensity and FWHM of the diffraction peaks. A systematic study of the effect of substrate temperature on crystallographic orientation for CSS CZT films indicated that for substrate temperatures above 520 °C, all films exhibited preferential orientation along the (111) direction, while at 500 °C, they exhibited random orientation.

### 3.2. Solar cells

Solar cells based on CZT were fabricated using deposition conditions that yielded the desired band gap range (1.65–1.75 eV). The cell structures resembled the typical CdTe superstrate configuration, with CdTe being replaced with CZT, i.e., glass/TCO/window layer/CZT/back contact. Back contacts based on Cu-containing graphite

paste and the transparent option of ZnTe/Cu were used. Several window layers were evaluated, although CdS remains one of the most successful window layers in thin film solar cells. It was anticipated that CZT-based solar cells may require a postdeposition heat treatment, similar to the CdCl<sub>2</sub> heat treatment used for CdTe; however, initially as-deposited solar cells were completed and characterized.

All as-deposited devices were found to exhibit poor solar cell characteristics. Their  $J$ – $V$  was dominated by extremely high series resistances that limited the FFs to below 40%; the high series resistance could be an indication of a compensated and highly resistive absorber. The  $V_{OC}$ 's were also low considering the band gap of the absorber (the highest  $V_{OC}$  obtained for CZT/CdS junctions was in the range of 770–790 mV). Spectral response measurements revealed what is believed to be the performance-limiting factor in CZT heterojunction solar cells. Typical spectral response data for several CZT devices fabricated on different window layers are shown in Fig. 5; all CZT films were deposited using CSS. As these data suggest as-deposited CZT junctions exhibit poor collection characteristics. The wavelength dependence indicates that carriers generated deeply in the CZT absorber suffer greater losses, suggesting that the electronic/transport properties of this material are not optimized, and bulk recombination must be minimized. The overall magnitude in the QE data shown in Fig. 5 was rather typical, with CZT/SnO<sub>2</sub> junctions always exhibiting higher QE (and therefore  $J_{SC}$ ). The variation in QE among the various window layers also suggests that interface recombination (wavelength independent) may also be present. Junctions formed with ZnSe exhibited even lower QE (below 10%). Although inefficient carrier collection is directly related to  $J_{SC}$ , it also affects the FF and  $V_{OC}$ ; improving the poor collection of these devices, it will improve all photovoltaic parameters. Junctions

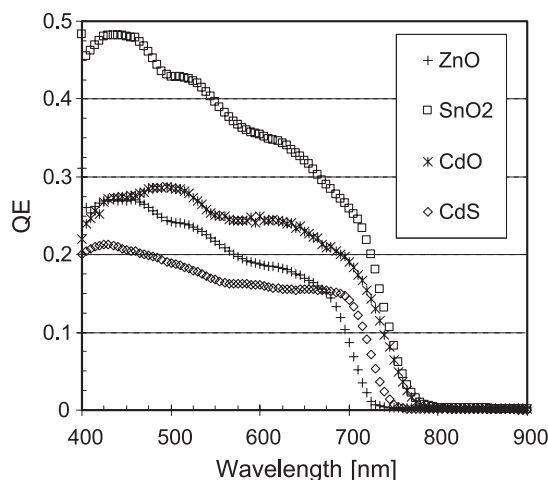


Fig. 5. Spectral response data for CZT junctions fabricated with different window layers.



fabricated using CZT deposited by sputtering exhibited the same trends shown in Fig. 5, with CZT/SnO<sub>2</sub> junctions yielding higher QE's; however, the overall performance for similar structures (i.e., based on CZT with the same band gap and same back contact), sputtered junctions were inferior to those prepared by CSS. This behavior could be partially explained by the structural characteristics of CZT films described in the previous section.

Due to the apparent limitations of as-deposited junctions, several heat treatments were employed in order to determine whether solar cell performance could be improved. These included simple heat treatments in He, H<sub>2</sub>, or O<sub>2</sub> ambient, and chloride-based treatments using CdCl<sub>2</sub> or ZnCl<sub>2</sub>. From spectral response measurements, it was determined that the use of CdCl<sub>2</sub> (process utilized for CdTe cells) resulted in a band gap shift in CZT. The absorption edge shifted toward longer wavelengths (lower energy). This behavior was interpreted as loss of Zn during the heat treatment. It has been previously found that CdCl<sub>2</sub> heat treatments of CZT films lead to formation of CdTe and ZnO, which is consistent with the observation in this work [5]. Replacing CdCl<sub>2</sub> with ZnCl<sub>2</sub> did not result in a band gap change (based on spectral response measurements); however, performance improvements were only marginal and in most cases well within experimental errors. The most consistently improved junctions were those heat-treated in a H<sub>2</sub> ambient; the time and temperature for the heat treatment were 10 min and 300–450 °C. The improvement in the spectral response for a CZT/CdS junction heat-treated in H<sub>2</sub> is shown in Fig. 6. It is believed that H<sub>2</sub> is responsible in partially improving the electronic properties of CZT leading to more efficient collection of photogenerated carriers. However, a better understanding the role of H<sub>2</sub> and its impact on the properties of the absorber and the

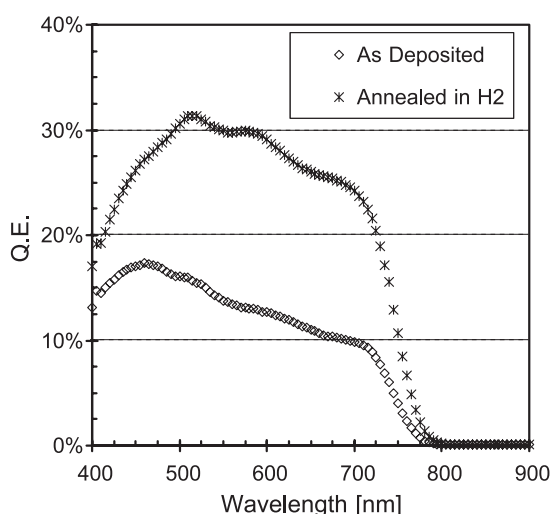


Fig. 6. Spectral response of a CZT/CdS junction before and after a heat treatment in H<sub>2</sub>.

Table 1

Summary of solar cell characteristics obtained for CZT solar cells fabricated with various window layers

$E_G$ [eV]	$V_{OC}$ [mV]	$J_{SC}$ [mA/cm <sup>2</sup> ]	Structure	Heat treatment
1.77	200–260	3.0–6.3	CZT/CdS/SnO <sub>2</sub>	H <sub>2</sub> /400 °C
1.73	670–790	1.0–1.5	CZT/CdS/SnO <sub>2</sub>	H <sub>2</sub> /400 °C
1.65	200	4.4–9.5	CZT/SnO <sub>2</sub>	H <sub>2</sub> /400 °C
1.72	180–220	6.7–8.5	CZT/SnO <sub>2</sub>	None
1.65	160–240	6.0–10.0	CZT/SnO <sub>2</sub>	None
1.67	570–600	1.0	CZT/ZnSe/SnO <sub>2</sub>	He/400 °C
1.71	360–500	0.2	CZT/ZnSe/SnO <sub>2</sub>	None
1.71	130–200	5.0–7.0	CZT/ZnO/SnO <sub>2</sub>	None

junction interface will require further investigations. A summary with typical CZT cell characteristics is provided in Table 1; the listed band gap values are estimates from extrapolations of the CZT absorption edge from spectral response data. Although CZT/SnO<sub>2</sub> junctions yielded the highest  $J_{SC}$ 's, the highest  $V_{OC}$ 's were obtained with CdS as the window layer, similar to what is observed with CdTe junctions.

#### 4. Summary/conclusions

Single-phase Cd<sub>1-x</sub>Zn<sub>x</sub>Te thin films, with a composition corresponding to a band gap of 1.65–1.75 eV, have been prepared by codeposition of CdTe and ZnTe using two deposition technologies: rf sputtering and close-spaced sublimation. Films deposited by CSS, exhibited better microstructure and overall crystallinity due to the high deposition temperatures associated with this process. Both processes yielded very good compositional and spatial uniformity, although in the case of CSS films, variations in composition along the thickness directions were often detected. As-deposited CZT solar cells exhibited poor characteristics primarily due the transport properties of the absorber and the quality of the CZT/window interface. Chloride-based treatments did not improve solar cell performance, and in the case of CdCl<sub>2</sub>, the band gap of CZT was found to decrease presumably due to loss of zinc. Improvements in collection and overall performance were demonstrated by annealing the devices in H<sub>2</sub> ambient. Although these improvements can be interpreted as a reduction in defects both within CZT and at the junction interface, further understanding of the transport properties of CZT and its interface with the window layer is necessary to further advance the performance of CZT-based solar cells.

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