Transparent conductors and buffer layers for CdTe solar cells

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Abstract

Thin film CdTe solar cells are typically of the supertrate configuration where the junction is fabricated on a glass substrate coated with a transparent conducting oxide that serves as the front contact. The most commonly used transparent contacts are SnO_2 and ITO, due to their electro-optical properties and chemical and thermal stability. Binary and ternary transparent oxides of Cd, In, Zn, and Sn have been prepared by sputtering and chemical vapor deposition, and their structural and electro-optical properties have been investigated. Most sputter-deposited films were deposited at room temperature and subsequently annealed in order to improve their structural and electrical properties. The performance of CdTe solar cells has been studied for various combinations of transparent oxides that included the use of bilayer structures, where a resistive or buffer layer was deposited on top of the conductive oxide. The use of a buffer layer has been found to improve solar cell performance in particular when the CdS thickness is relatively small. Several resistive oxides have been found to be effective buffer layers. These include SnO_2, In_2O_3, and Zn_2SnO_4. Conductive oxides utilized in this work include SnO_2, ITO, $CdIn_2O_4$, and Cd_2SnO_4.
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1. Introduction

Cadmium telluride (CdTe) is a leading material for thin film photovoltaics, and several laboratories have fabricated CdTe/CdS solar cells with efficiencies over 15% [1–3]. Further advancement of device efficiencies has been difficult and hindered by several factors. The use of a thin CdS layer is one approach to advance device efficiencies, by enhancing the short-circuit current density (J_{SC}). Since carrier collection in CdS is not efficient, essentially all light absorbed in this layer (which translates to approximately 7 mA/cm^2 in J_{SC}) is lost. However, this approach is faced with significant challenges. As the thickness of CdS is reduced, the open-circuit voltage (V_{OC}) and fill factor (FF) decrease, and essentially compensate gains in J_{SC}. One of the suspected reasons for the decrease in the FF and V_{OC} is believed to be the formation of CdTe/TCO microjunctions which have significantly inferior characteristics than CdTe/ CdS and essentially act as shunts to the main junction (i.e. CdTe/CdS). The use of a high resistive (high-ρ), also referred to as buffer layer, at the front contact has been found to be an effective way to maintain high V_{OC}s and FFs while utilizing thin CdS. It has been recently suggested that the use of a high-ρ layer adjacent to the CdS serves as a high bandgap extension of the thin CdS layer [4]. In this paper, the performance of CdTe/CdS junctions fabricated with thin CdS (80–100 nm), on various low-ρ/high-ρ bilayer transparent oxides, is reviewed. The low-ρ transparent oxides used include SnO_2:F and ITO, the most commonly used with CdTe solar cells, and Cd_2SnO_4 and $CdIn_2O_4$; these were used in bilayer structures (i.e. glass/ low-ρ/high-ρ) with SnO_2, In_2O_3, and Zn_2SnO_4 as the high-ρ layers.

2. Experimental

The primary method of deposition for the transparent conductive (low-ρ) and resistive (high-ρ) oxide layers discussed in this paper is rf magnetron sputtering. Ternary

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Table 1
Summary of deposition conditions for all low-ρ and high-ρ films

High- or low-ρ	Deposition method—comments
ITO (low-ρ)	Rf-sputtering of 90% In_2O_3/10% SnO_2 (99.99%) in Ar; deposited at RT and heat-treated in inert ambient
SnO_2:F (low-ρ)	MOCVD; TMT; O_2; CBrF3; He carrier gas; deposited at 480 °C
Cd_2SnO_4 (low-ρ)	Rf co-sputtering of CdO and SnO_2 (99.99%) in Ar; deposited at room temperature and heat-treated in inert ambient
$CdIn_2O_4$ (low-ρ)	Reactive rf co-sputtering of Cd and In (99.99%) in Ar/O_2 (25%); deposited at room temperature and heat-treated in inert ambient
SnO_2 (high ρ)	Reactive sputtering of Sn (99.99%) in Ar/O_2 (25%); deposited at 300 °C
In_2O_3 (high ρ)	Reactive sputtering of In (99.99%) in Ar/O_2 (25%); deposited at 300 °C
Zn_2SnO_4 (high ρ)	Rf sputtering of SnO_2 and ZnO (99.99%) in Ar; deposited at 25–425 °C and heat-treated in inert ambient

compounds such as Cd_2SnO_4 and Zn_2SnO_4 were deposited by co-sputtering. Two 3-in. magnetron sputtering sources, model Kurt J. Lesker Taurus TRS3FSA, were mounted at the baseplate of a vertical 18-in. bell jar vacuum system. The power was supplied by Advanced Energy RFX-600 power supplies. A rotating round substrate holder, 12 cm in diameter, was mounted approximately 10 cm from the sputtering sources. To improve thickness uniformity, the sputtering sources were tilted in such a way that the source axis formed an angle of approximately 22.5° with the normal to the plane of the substrate holder. Most depositions were carried out at room temperature; exceptions will be noted in the discussion section. Argon or an Ar/O_2 mixture was used as the sputtering ambient. The system baseline pressure was 10^{-6} Torr, and sputtering was carried out at 3.0 ± 0.2 mTorr. The films were deposited on borosilicate glass substrates (Corning 7059), which were cleaned in a dilute solution of hydrofluoric acid (H_2O/HF 10:1) prior to the deposition. Table 1 lists the compounds used for the fabrication of bilayers, which subsequently were processed into CdTe thin film solar cells. For solar cell fabrication, the semiconductors CdS and CdTe were deposited by chemical bath deposition and close-spaced sublimation, respectively [3]. The glass/low-ρ/high-ρ/CdS/CdTe structures were heat-treated in the presence of $CdCl_2$ prior to the application of a back contact, which was formed by applying graphite paste doped with HgTe/Cu to the surface of the CdTe, and heat-treated in inert ambient at 270 °C. Solar cells were characterized using standard current–voltage and spectral response measurements. The solar simulator based on ELH lamps was calibrated at AM1.5 (100 mW/cm^2). Monochromatic light J–V measurements were also performed. Thin films were characterized using Hall effect, four-point probe, optical transmission, and X-ray diffraction measurements.

3. Results

3.1. Thin films

The electro-optical and structural properties of the ternary compounds (such as $CdIn_2O_4$ and Cd_2SnO_4) were investigated and optimized as a function of the metal ratios (Cd/In and Cd/Sn). All room-temperature deposited films were amorphous and crystallized after annealing in inert ambient. The temperature of crystallization varied depending on the material. Crystallization of Cd_2SnO_4 was verified with XRD measurements at 550 °C, for Zn_2SnO_4 at 600 °C, and for $CdIn_2O_4$ at 400 °C. Table 2 summarizes the properties of the low-ρ films utilized in this study including the most commonly used front contact materials for CdTe cells ITO and SnO_2:F. The resistivity, mobility, and carrier concentration data are based on Hall effect measurements; the four-point probe technique was also used to verify the resistivity values. In the case of $CdIn_2O_4$, the lowest resistivity was obtained for films prepared under In-rich conditions (a starting Cd/In ratio of 0.37) and which were found to contain a secondary phase of In_2O_3 [5]. For Cd_2SnO_4, the lowest resistivity was obtained for films prepared under Cd-rich conditions. Additional information on the electro-optical and crystallographic characteristics of $CdIn_2O_4$ and Cd_2SnO_4 can be found elsewhere [5,6]. The resistivity of as-deposited high-ρ films was typically too high to measure with the four-point probe technique. After annealing in inert ambient (which promoted crystallization of the amorphous as-deposited films), the resistivity was in the 0.01–2 Ω cm range. Selection of the "optimum" deposition conditions for the high-ρ films was primarily based on their crystalline structure, as preliminary device work indicated that if these were used in their amorphous state, solar cell performance was poor.

3.2. Solar cells

Record performance thin film CdTe solar cells have been fabricated with thin CdS layers on bilayer (low-ρ/high-ρ) structures, demonstrating the need for a high-ρ or buffer transparent layer at the front contact [1,3]. As a reference point for the results to be reviewed in this paper, Fig. 1 shows the light J–V characteristics of two CdTe cells fabricated on SnO_2:F one with and the other without a high-ρ layer. The improvement in both the FF and V_{OC}

Table 2
Properties of conductive (low-ρ) oxides used in this work

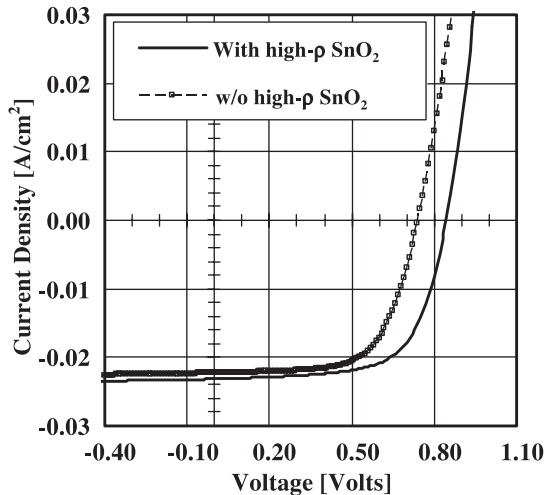| Material	Resistivity [Ω cm]	Mobility [cm^2 V^{-1} s^{-1}]	Carrier Concentration [cm^{-3}]	Average %T (400–900 nm)
SnO_2:F	4.0×10^{-4}	38.0	4.0×10^{20}	84
ITO	2.0×10^{-4}	32.0	1.0×10^{21}	90
Cd_2SnO_4	2.0×10^{-4}	29.2	8.5×10^{20}	92
$CdIn_2O_4$	2.9×10^{-4}	30.9	5.5×10^{20}	90

Fig. 1. Light $J–V$ characteristics of CdTe/CdS solar cells fabricated with and without a high-ρ SnO$_2$ layer; differences in J_{SC} are primarily due to uncertainties in area measurements.

(approximately 6% and 90 mV higher) for the device fabricated on the bilayer structure is apparent. Spectral response measurements of these cells were essentially identical with J_{SC}'s being approximately 23.40 mA/cm^2 for both devices (without AR coating). The shunt resistance (estimated at −1.5 V) was lower for the device without the resistive layer (1000 vs. 2800 Ω cm^2). These values may not necessarily represent the shunt resistances but rather could be related to collection as it will be discussed later. The remainder of this section describes solar cell results for several low-ρ/high-ρ combinations of the materials listed in Table 1.

3.2.1. SnO$_2$:F(MOCVD)/SnO$_2$(sputtered)

Reactively sputtered SnO$_2$ (from Sn) was considered as the high-ρ layer due to the potential manufacturing advantages of this process. For cell fabrication, the only variation in the characteristics of the bilayer was the thickness of the reactively sputtered SnO$_2$ (12.5, 25, 50, and 100 nm) which was deposited at 300 °C (see Table 1). This temperature was chosen based on preliminary device results and film crystallinity. The resistivity was found to be approximately 2.50×10^{-2} Ω cm, and XRD measurements revealed only a peak corresponding to the (110) direction, indicating the preferential orientation of the reactively sputtered SnO$_2$. Device characteristics for CdTe cells fabricated with SnO$_2$:F(MOCVD)/SnO$_2$ (sputtered) bilayers are summarized in Fig. 2 as a function of the high-ρ layer thickness. In all cases, device performance surpasses that of the reference (no high-ρ layer) device discussed in the previous section. Apparently variation in the thickness of the high-ρ SnO$_2$ has not resulted in any consistent trends, suggesting that even at the small thickness of 12.5 nm this layer can be an effective high-ρ (buffer) layer. Fig. 3 shows the SR for the same devices, suggesting that current generation is nearly identical with the only exception being
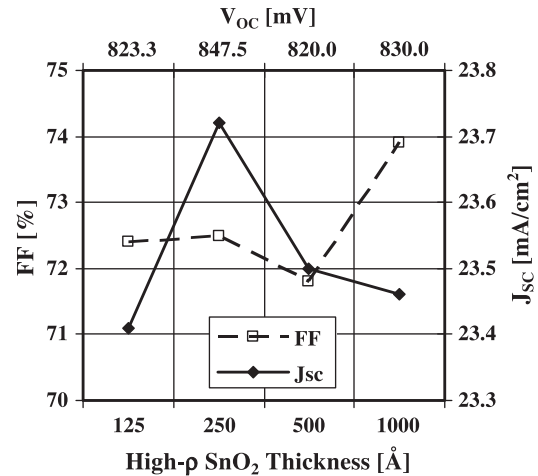

Fig. 2. Cell performance as a function of the thickness of the (reactively sputtered) high-ρ SnO$_2$ layer.

the device with 25 nm SnO$_2$ that exhibits improved collection at long wavelengths (700–850 nm).

3.2.2. ITO/In$_2$O$_3$

Indium tin oxide (ITO) is another widely used front contact material for CdTe solar cells. Although in many cases it has been found to be very effective, it has also been shown to form rectifying front contacts [7]. This was interpreted as a surface effect, as the work function of ITO has been found to vary from 4.0 to 5.0 eV, depending on the concentration of O$_2$ at the surface of the film [8]. Fig. 4 shows the light $J–V$ characteristics for CdTe cells fabricated on ITO/In$_2$O$_3$ bilayers, at various In$_2$O$_3$ thicknesses. The $J–V$ behavior around V_{OC}, of the cell fabricated on ITO without the high-ρ In$_2$O$_3$, suggests that the front contact (i.e. ITO/CdS) is rectifying and seems to support the findings of others discussed above [7,8]. The inclusion of the high-ρ In$_2$O$_3$ (thickness 25–200 nm) results in devices with essentially identical characteristics; the main variations among these cells are in series resistance, but these are
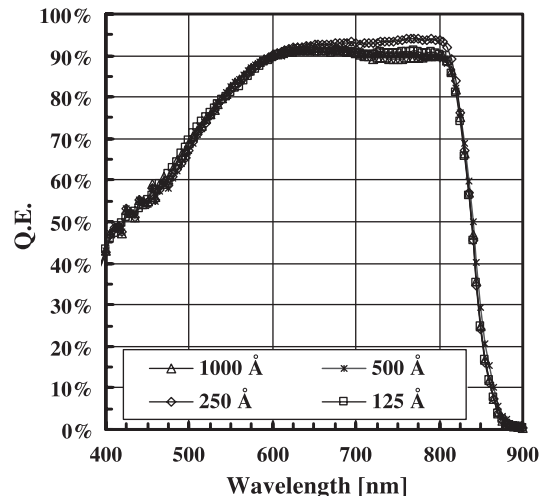

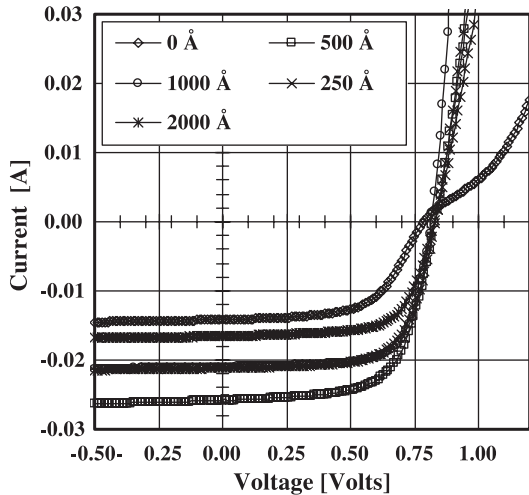
Fig. 3. Spectral response of the devices of Fig. 2.

Fig. 4. Light J–V characteristics for cells fabricated on ITO/In$_2$O$_3$ bilayers.

small and do not correlate with the thickness of In$_2$O$_3$. In order to further evaluate the effectiveness of In$_2$O$_3$ as a buffer layer, a series of cells with varying CdS and In$_2$O$_3$ thicknesses were fabricated; V_{OC}s and FFs are summarized in Fig. 5. In general, the thickness of In$_2$O$_3$ seems to have a rather minor effect on performance (with one exception); however, as the thickness of the CdS is decreased performance degrades consistently, clearly demonstrating the key problem when thin CdS films are utilized in CdTe solar cells. Nevertheless, In$_2$O$_3$ appears to be an effective buffer layer; for this specific case (used with ITO), it is also beneficial in improving the contact with CdS, eliminating the rectifying behavior obtained for cells fabricated directly on ITO, by presumably affecting the O$_2$ concentration on the ITO surface.

3.2.3. Ternary oxides

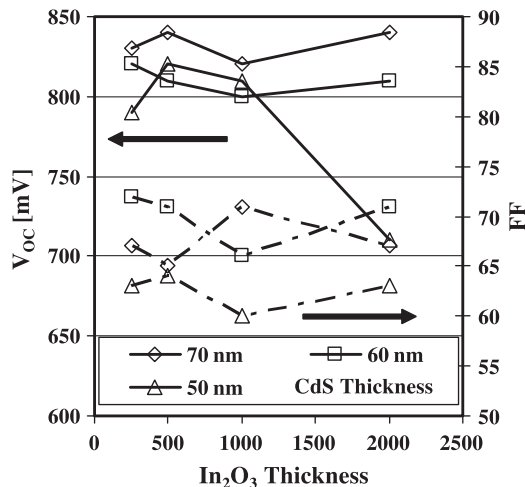This group of materials was considered as they have been used for the fabrication of CdTe cells with record

efficiencies [1]. In addition to Cd$_2$SnO$_4$ (low-ρ) and Zn$_2$SnO$_4$ (high-ρ), CdIn$_2$O$_4$ (low-ρ) was also used for solar cell fabrication. Devices fabricated on CdIn$_2$O$_4$ without a high-ρ layer resulted in solar cell performance similar to that described in a previous section for SnO$_2$:F (V_{OC}s in the range of 700–760 mV and FFs in the low 60s). When CdIn$_2$O$_4$ was used in bilayer structures with SnO$_2$ or In$_2$O$_3$, cell performance improved with V_{OC}s and FF reaching 840 mV and 71%, respectively, once again demonstrating the improvements in device performance when high-ρ buffer layers are used. In general, devices fabricated using CdIn$_2$O$_4$ exhibited similar performance to that obtained for other materials such as the commonly used SnO$_2$; however, CdIn$_2$O$_4$ was found to be optically superior to SnO$_2$ (see Table 2).

The current record efficiency CdTe cells have been fabricated using Cd$_2$SnO$_4$ as the front contact material [1]. For this work, the potential of Cd$_2$SnO$_4$ films was investigated in bilayer structures with high-ρ films. Devices were also fabricated directly on Cd$_2$SnO$_4$; both the V_{OC}s and FFs were the highest among all solar cells fabricated without a high-ρ layer. In fact when Cd$_2$SnO$_4$ was used in a bilayer structure, with SnO$_2$ as the high-ρ layer, solar cell performance remained essentially unchanged. Table 3 summarizes cell results for CdTe/CdS cells fabricated on Cd$_2$SnO$_4$/SnO$_2$ bilayers. All results presented prior to this point suggested that a high-ρ layer enhanced device performance (for the range of CdS thicknesses used). It is not clear at this time why Cd$_2$SnO$_4$-based devices do not benefit from the use of a high-ρ layer. However, since these films are initially amorphous (and resistive), it can be speculated that they do not fully recrystallize during the post-deposition heat treatment, leaving the surface of Cd$_2$SnO$_4$ more resistive than the bulk. Nevertheless, further studies are necessary to better understand the properties of the front contact/CdS interface and how it affects device performance. Finally, the most promising combination of low-ρ/high-ρ materials was found to be Cd$_2$SnO$_4$/Zn$_2$SnO$_4$. Although the record efficiencies reported by others were not reproduced, this combination resulted in the most significant improvement in J_{SC} without losses in V_{OC} (typical of CdTe cells). Fig. 6 shows the SR of a CdTe cell fabricated on Cd$_2$SnO$_4$/Zn$_2$SnO$_4$. A unique feature of these devices is the fact that the blue response suggests that the thickness of CdS has been greatly reduced (although the initial thickness of

Fig. 5. V_{OC} and FF as a function of the CdS and In$_2$O$_3$ thicknesses.

Table 3
Characteristics of Cd$_2$SnO$_4$-based CdTe solar cells

High-ρ	V_{OC} [mV]	FF [%]	J_{SC} [mA/cm^2]
None	821	69.6	23.1
Sputtered SnO$_2$ (reactively from Sn)	825	69.7	23.6
Sputtered SnO$_2$ (from SnO$_2$)	830	68.1	23.1
SnO$_2$ by MOCVD	849	68.9	23.9

CdS was similar to devices discussed previously, i.e. 80 nm); the red response also suggests that collection of deeply generated carriers is very efficient. Although a portion of the CdS is always consumed during the fabrication of CdTe cells, in this case it appears that nearly all CdS has been consumed. It has been previously shown that interdiffusion between CdS and Zn_2SnO_4 takes place at high temperatures or during the $CdCl_2$ heat treatment [9]. Therefore for the cells of Fig. 6 the final thickness of CdS is greatly reduced due to interdiffusion of the CdS with CdTe and Zn_2SnO_4. The V_{OC}, FF, and J_{SC} for these cells were 825–830 mV, 68–69%, and 24.5–24.9 mA/cm^2.

3.3. Monochromatic J–V measurements—collection

In addition to AM1.5 light J–V measurements, some devices were also characterized using monochromatic light J–V measurements using 20 nm bandwidth interference filters, and adjusting the light intensity to achieve approximately AM1.5 equivalent intensity (within the specific 20 nm bandwidth). The wavelengths used were 450, 520, 640, and 800 nm. Short wavelength light (i.e. 450 and 520 nm) is strongly absorbed in CdTe and therefore the photogenerated carriers can be readily collected by the junction field. As the wavelength increases, the photo-generated carriers are created deeper into CdTe and can suffer recombination losses depending on the strength of the collecting field and the material properties (i.e. carrier lifetimes). Fig. 7 shows the FF of several CdTe solar cells as a function of wavelength. The dotted lines mark the corresponding white light FFs. The devices were fabricated using SnO_2 and In_2O_3 as the high-ρ layers; a device without a high-ρ layer is also shown. In all three cases, the FF decreases with wavelength from values that reach the high 70s for 460 nm light, to low 60s and 50s for 800 nm light, suggesting that the collection efficiency decreases for deeply generated carriers; the white light FFs lie between
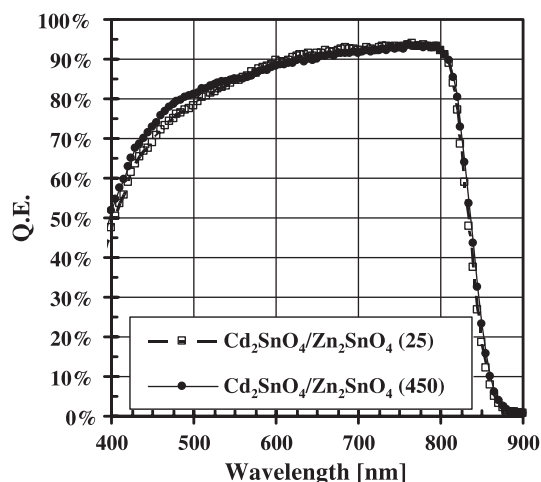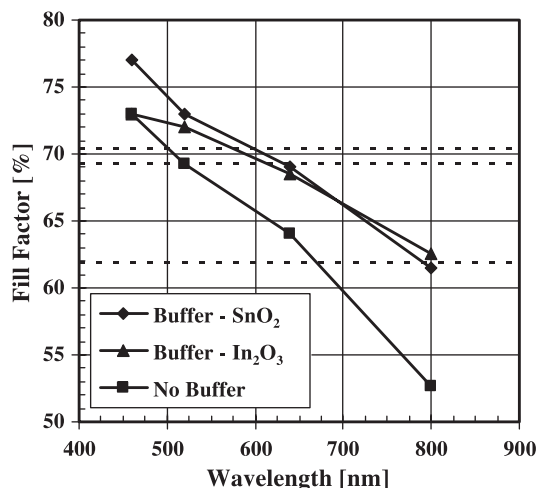

Fig. 7. The FF as a function of wavelength for several CdTe cells fabricated with low-ρ/high-ρ bilayers.

the two extremes for all three cells. The collection efficiency for the device fabricated without a high-ρ layer decreases more than the other two cells, even though its short wavelength (450 nm) FF is well above 70. It should be noted that the observed decrease in the FF with wavelength is not related to light intensity and/or device shunting effects; additional monochromatic light J–V measurements were carried out at various light intensities and the FF dependence on wavelength was found to be the same (as shown in Fig. 7), while the light shunt resistance calculated from the slope of the J–V at reverse bias (−2 V) exhibited no or very small dependence on wavelength. These results suggest that the FF in all CdTe cells is limited by inefficient collection which improves with the inclusion of a high-ρ layer at the front contact. It is therefore suggested that the high-ρ layer appears to support a stronger collecting field within the CdTe which leads to improved collection.

4. Conclusions

The effect of various sputter-deposited low-ρ/high-ρ transparent oxides on the performance of CdTe solar cells fabricated with CdS films of thicknesses less than 90 nm has been studied. In nearly all cases, the use of a high-ρ (buffer) oxide layer leads to improved device performance. When a high-ρ layer was incorporated in devices fabricated on ITO, this lead to improving the otherwise rectifying contact between CdS and ITO. Monochromatic color J–V measurements suggest that in all device configurations studied the FF of CdTe solar cells is collection limited. The use of a high-ρ layer improved collection for deeply absorbed light, suggesting that the high-ρ layer may be affecting the strength of the collection field within CdTe. The Cd_2SnO_4/Zn_2SnO_4 bilayer structure was found to be the most effective, as high V_{OC}s and relatively high FFs were achieved for very small CdS thicknesses.

Fig. 6. Spectral response of CdTe cells fabricated on Cd_2SnO_4/Zn_2SnO_4 bilayers.

Acknowledgement

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