Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 6060–6063
thin solid films
www.elsevier.com/locate/tsf

The structural and electrical properties of Zn–Sn–O buffer layers and their effect on CdTe solar cell performance

S. Gayam, S. Bapanapalli, H. Zhao, L. Nemani, D.L. Morel, C.S. Ferekides *

Center for Clean Energy and Vehicles, Department of Electrical Engineering, University of South Florida, Tampa, FL 33620, United States

Available online 19 December 2006

Abstract

Thin films of zinc–tin–oxide (ZTO) have been deposited on SnO_2:F coated glass substrates by co-sputtering of SnO_2 and ZnO. The deposition conditions for ZTO were controlled in order to vary film stoichiometry. The electro–optical and structural properties of ZTO have been studied as a function of their stoichiometric ratio and post-deposition annealing conditions. The same films were subsequently utilized as part of a bi-layer transparent front contact for the fabrication of CdTe solar cells: glass/SnO_2:F/ZTO. The performance of these devices suggested that the ZTO deposition and cell processing conditions can be optimized for enhanced device performance in particular for devices with thin CdS. Specifically, high blue spectral response (>70% at 450 nm), accompanied by high open-circuit voltages (830 mV), and fill factors (70^+%) have been demonstrated. Best solar cell performance was obtained for multi-phase ZTO films deposited at substrate temperatures of 400°C and a Zn/Sn ratio of 2.0, and which contained the binary phase of ZnO_2.

Keywords: Zinc tin oxide; CdTe; Solar cells

1. Introduction

The front transparent contact of both leading thin film PV technologies, CIGS and CdTe, has the form of a bi-layer: a high conductivity/high resistivity bi-layer where the high resistivity component is also referred to as a buffer. Although, various explanations have been provided on the role of this buffer, it is clear that it enhances solar cell performance. For CdTe solar cells, the work at the National Renewable Energy Laboratory where Zn_2SnO_4 has been used as a buffer has lead to record efficiencies for this technology [1]. One of the unique characteristics of the Zn_2SnO_4 buffer is that it interdiffuses with the window CdS leading to thinner CdS films in the finished device and therefore improved spectral response in the blue region (<500 nm) [2]. In the absence of such a buffer layer, solar cell performance, and in particular the V_{oc} and FF, decrease as the thickness of the CdS window layer is decreased. The main objective of this work is to study the properties of Zn–Sn–O (ZTO) thin films, and how these affect the performance of CdTe

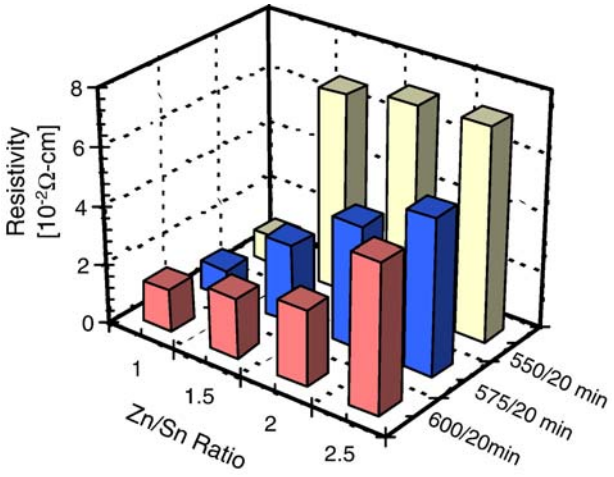

Fig. 1. The resistivity of ZTO films deposited on glass as a function of the Zn/Sn ratio and the annealing temperature.

* Corresponding author. Tel.: +1 813 974 4818; fax: +1 813 974 5250.
E-mail address: ferekide@eng.usf.edu (C.S. Ferekides).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.12.165

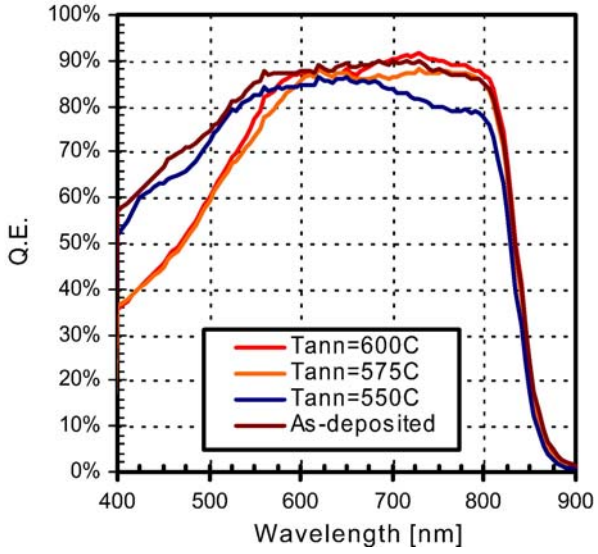

Fig. 2. QE for CdTe cells fabricated on ZTO films annealed at different temperatures (prior to the CdTe deposition).

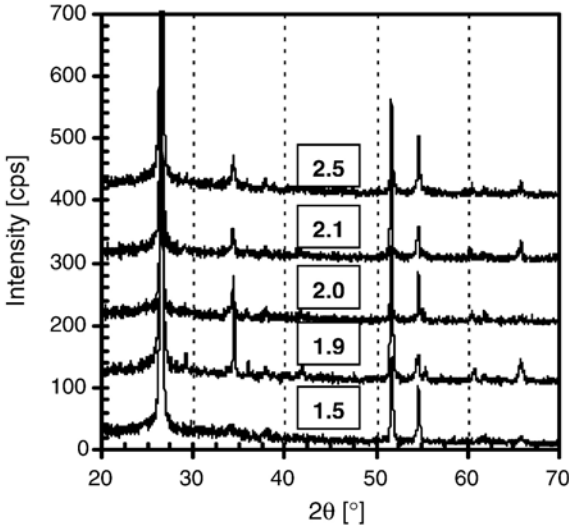

Fig. 3. XRD spectra of ZTO films deposited (on SnO_2) with different Zn/Sn ratios (T_{DEP}=RT; T_{ANN}=600 °C).

solar cells, in particular devices fabricated with a thin CdS window layer, and therefore enhanced blue response.

2. Experimental

Thin films of Zn–Sn–O (ZTO) have been deposited by co-sputtering from the binary oxides (ZnO and SnO_2 with 5N purity. Variations in the deposition conditions included the individual deposition rates to control film stoichiometry (Zn/Sn ratio from 1.0 to 2.5), ambient (Ar vs. Ar/O_2), and substrate temperature (room temperature and 400 °C; 400 °C is the upper limit of the heater/substrate holder assembly in the deposition chamber used for this work). Typically the ZTO films were annealed in the temperature range of 550–625 °C in inert or O_2 ambient. Most ZTO films were deposited on borosilicate-glass/SnO_2:F substrates, with a small number of films deposited on plain glass substrates in order to perform resistivity measurements. Solar cells discussed in this paper had the typical CdTe superstrate configuration with the front contact having a bi-layer structure with a conductive SnO_2:F film and high resistivity ZTO buffer: glass/SnO_2:F/ZTO/CdS/CdTe/back contact. The CdS was deposited by chemical bath deposition (CBD), the CdTe by the close-spaced sublimation (CSS), and the back contact was Cu-doped graphite [3]. The starting thickness of the CdS was approximately 80–90 nm; CdTe thickness was in the 4–5 μm range. The $CdCl_2$ heat treatment annealing temperature was in certain instances varied to enhance or limit the consumption of CdS that takes place due to interdiffusion with the CdTe and ZTO films. The ZTO structural properties were studied using X-ray diffraction (XRD) and their resistivity was measured using the four-point probe method; optical transmission was measured in the 400–900 nm range using a spectrometer/integrating sphere system. Solar cells were characterized using standard solar cell techniques.

3. Results and discussions

3.1. Resistivity and optical transmission of ZTO

The resistivity of ZTO films deposited on glass was measured as a function of the Zn/Sn ratio and the post-deposition annealing temperature. Fig. 1 shows the resistivity of ZTO as a function of these two parameters (annealing ambient: He); most results presented in this paper are based on films annealed in He ambient as this condition was found early on to yield superior solar cell performance. For Zn/Sn ratios of 1.5 and higher the resistivity increases with the Zn/Sn ratio, and it decreases with increasing annealing temperature. The effect of the ratio on resistivity is in general agreement with the work of others who attributed the resistivity of ZTO to the various material phases found in the films [4]; at this time it is not known whether the entire film has fully crystallize or whether it contains an amorphous phase which could further influence the film resistivity. The higher resistivity at the low annealing temperatures can be attributed to the fact that the as-deposited films are

Table 1
Solar cell characteristics for devices with ZTO films annealed at different temperatures (Zn/Sn=2.0)

ZTO annealing temp. [°C]	V_{oc} [mV]	FF [%]	J_{sc} [mA/cm^2]	R_{SH} [Ω-cm^2]
None	730	58.0	23.40	1100
550	730	55.0	22.00	1000
575	820	68.0	21.40	1170
600	830	69.0	22.00	900

Table 2
Zn–Sn–O phases identified in the films of Fig. 3

Zn/Sn	Zn_2SnO_4	$ZnSnO_3$
1.5	None	(006)
1.9	(220), (311), (222), (400), (440)	(006)
2.0	(311), (222), (400), (440)	(006)
2.1	(311), (222)	None
2.5	(311), (222)	(006)

Table 3
Solar cell characteristics for devices fabricated with ZTO films deposited at different Zn/Sn ratios

Zn/Sn ratio	V_{oc} [mV]	FF [%]	J_{sc} [mA/cm^2]	QE at 450 nm	R_{SH} [Ω-cm^2]
1.5	710	54.6	24.40	0.70	500
1.9	770	44.3	24.00	0.80	730
2.0	780	58.2	24.50	0.75	800
2.1	810	66.6	23.10	0.57	800
2.5	790	66.7	23.00	0.60	900

amorphous and remain as such for annealing temperatures up to 550 °C; they begin to crystallize at approximately 575 °C [5]. The optical transmission of the ZTO films was measured in the range of 400–900 nm for as-deposited and annealed films with Zn/Sn ratios from 1.5 to 2.5. The average transmission in this range was approximately 92–94%, with films annealed at 600 °C exhibiting higher transmission (up to 4% higher).

3.2. Structural properties of ZTO and CdTe solar cell performance

The effect of the annealing temperature on the crystallographic properties of ZTO films deposited on SnO_2/glass substrates at room temperature with a Zn/Sn ratio of 2.0 has been previously reported [5]; it was found that the as-deposited films are amorphous and they become polycrystalline at 575 °C (Zn_2SnO_4 was identified by XRD). Solar cells were fabricated on ZTO/SnO_2:F/glass substrates, for which the ZTO films were annealed at different temperatures (550–600 °C). The spectral response for four representative cells is shown in Fig. 2. Based on the blue response it appears that the final thickness of the CdS window layer is smaller for the devices with amorphous ZTO (as-deposited and annealed at 550 °C). Since the starting CdS thickness for all these devices was identical, it is suggested that for amorphous ZTO films the consumption of CdS due to interdiffusion (with ZTO) is significantly enhanced, leading to higher blue response. Nevertheless, the overall cell performance decreases due to losses in V_{oc} and FF as shown in Table 1; higher dark currents were one of the reasons for the lower performance. Therefore in this case the ZTO buffer layers did not prove to be effective for cells with small CdS thicknesses.

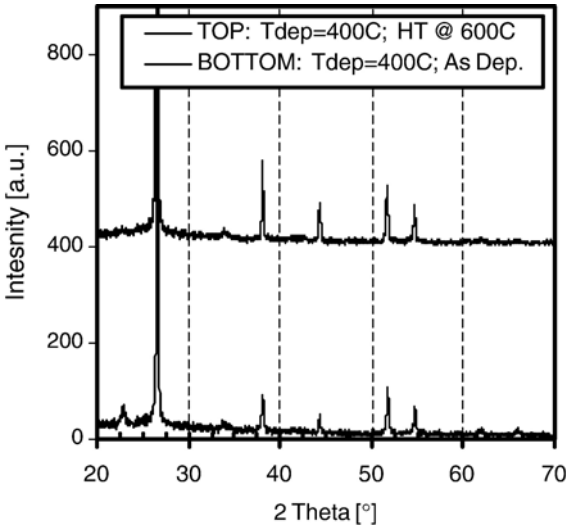

Fig. 4. XRD spectra of ZTO films deposited at 400 °C (Zn/Sn=2.0).

Table 4
Phases and directions identified in ZTO films deposited at 400 °C (Zn/Sn=2.0)

T_{ANN} [°C]	Zn_2SnO_4	$ZnSnO_3$	ZnO_2
600	(311)	(006)	(211)
none	(311)	(012); (006)	(211)

Fig. 3 shows the XRD spectra of ZTO films deposited (at room temperature) with different Zn/Sn ratios and annealed at 600 °C in He. It should be noted that since these measurements are for films deposited on glass/SnO_2 substrates, the potential formation of the SnO_2 phase in the ZTO films cannot be identified. The peaks located at 2Θ values of 26.63, 51.80, and 54.78° correspond to the glass/SnO_2 substrate. Table 2 lists the material phases and the corresponding directions identified for the films shown in Fig. 3; the locations for some of the strongest reflections for the ZTO films are also marked: Zn_2SnO_4 is marked with filled circles (●) and $ZnSnO_3$ with open circles (ϒ). As the data indicates in nearly all instances the ZTO films contain both zinc stannate phases: Zn_2SnO_4 and $ZnSnO_3$. These substrates were subsequently processed into solar cells; their performance characteristics are listed in Table 3. The two devices fabricated on substrates with Zn/Sn ratios of 2.1 and 2.5 exhibited very similar characteristics, while the performance of the other three (smaller ratios) decreased with the Zn/Sn ratio. Spectral response measurements for the three cells with the smaller Zn/Sn ratios revealed a higher blue response (0.70 or greater at $\lambda < 500$ nm), suggesting that the CdS films in those were thinned substantially during the solar cell fabrication process, presumably due to interdiffusion with both the CdTe absorber and the ZTO buffer. Since the starting thickness of CdS and all other processing conditions were identical for these cells (Table 3), it is suggested that the composition of the ZTO film is an important parameter influencing the consumption of the CdS film during the cell fabrication process; at this time it is not clear which one of the two zinc stannate phases plays a key role in this process, or whether the ZTO films were fully crystallized (i.e. no amorphous material present in the films). Nevertheless, regardless of the high blue response for these devices, it is apparent that the overall performance suffers due to the losses in V_{oc} and FF, which is typical of CdTe solar cells fabricated on thin CdS films; this is similar to what was described above for the cells listed in Table 1. Dark J–V measurements resulted in lower dark currents for the two largest Zn/Sn ratios indicating that the CdTe junctions fabricated on the corresponding ZTO films were superior.

Table 5
Solar cell characteristics for CdTe cells fabricated with ZTO films deposited at 400 °C and which exhibited high blue QE

V_{oc} [mV]	FF [%]	J_{sc} [mA/cm^2]	R_{SH} [Ω cm^2]
840	68.2	24.40	1700
830	71.0	23.80	1700
830	69.3	24.74	1900

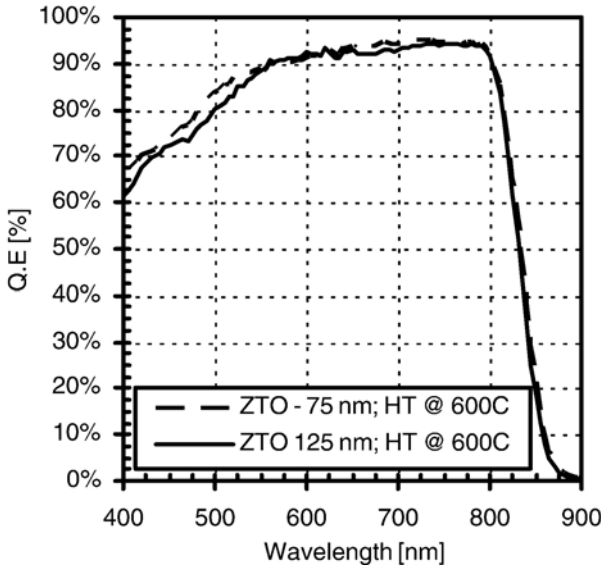

Fig. 5. QE of CdTe cells fabricated on ZTO films deposited at 400 °C.

All ZTO films discussed above were deposited at room temperature (and subsequently heat treated). The substrate deposition temperature for ZTO films was found to be an important process parameter. The XRD spectra for as-deposited (bottom) and heat treated (top) ZTO films co-deposited at 400°C with a Zn/Sn ratio of 2.0 are shown in Fig. 4. Unlike the films previously which comprised of the zinc stannate phases (Zn_2SnO_4, $ZnSnO_3$), the films in Fig. 4 also contain the binary ZnO_2 phase (marked with x) as shown in Table 4. Post deposition annealing does not appear to have an effect on the composition of the films as data in Fig. 4 suggests. A series of solar cells were fabricated on ZTO/SnO_2:F/glass substrates with ZTO films prepared under the same conditions as those shown in Fig. 4. Solar cell performance characteristics and the spectral response for these devices are shown in Table 5 and Fig. 5 respectively. It is apparent that the blue QE of all these devices is quite high (>65% for $\lambda < 500$ nm) in all cases, due to significant consumption of the CdS window layer. Most importantly the V_{oc} and FF of these cells are also high even at these small CdS thicknesses. Therefore, in this case the ZTO films function as affective buffer layers, i.e. high V_{oc}·s and FF's were maintained at small CdS thicknesses. It is clear from the device results presented above, that ZTO films can be effective buffers only when processed under certain conditions. At this time based on the results discussed in this paper, the key property of ZTO films appears to be their composition and potentially the presence of certain phases. It should be noted that the best device performance (for thin CdS films) was obtained when the ZTO films contained the binary phase of ZnO_2. The role of this phase and whether it is indeed the determining parameter will require further investigation. Studying the composition of the interfacial layers in finished devices would also reveal important information to further explain the role of the ZTO buffer and how it can be best utilized in the fabrication of efficient CdTe solar cells.

It should also be noted that solar cells fabricated on ZTO films annealed in O_2-ambient consistently yielded lower performance than cells fabricated on films annealed in inert ambient, which is the main reason the results presented in this paper have focused on ZTO films annealed in inert ambient. Films deposited in Ar-only ambient also yielded poor performance. All films discussed here were prepared in Ar/O_2 (25%O_2) and subsequently annealed in inert ambient.

4. Conclusion

The effect of film stoichiometry, deposition temperature, and post-deposition heat treatment of Zn–Sn–O films on CdTe solar cell performance has been investigated. It has been found that reasonable solar cell performance can be achieved for multi-phase Zn–Sn–O films. Films that only contained the zinc stannate phases (Zn_2SnO_4 and $ZnSnO_3$) yielded devices with reasonable performance. However, films that in addition to the two zinc stannate phases also contained a ZnO_2 phase yielded the best performance along with the highest blue response of approximately 75% (at 450 nm) with no apparent loss in V_{oc} or FF. These results clearly indicate that Zn–Sn–O buffers have the potential to be used with thinner CdS window layers, as long as the appropriate film composition is achieved.

Acknowledgement

This work was supported by the National Renewable Energy Laboratory (NREL). The authors would also like to thank Dr. Robert Mamazza for the modification and calibration of the sputtering unit used to prepare the ZTO films.

References

[1] X. Wu, J.C. Keane, R.G. Dhere, C. DeHart, D.S. Albin, A. Duda, T.A. Gessert, S. Asher, D.H. Levi, P. Sheldon, Proceedings of 17th European Photovoltaic Solar Energy Conference, 2001, p. 531.
[2] X. Wu, S. Asher, D.H. Levi, D.E. King, Y. Yan, T.A. Gessert, P. Sheldon, J. Appl. Phys. 89 (8) (2001) 4564.
[3] C.S. Ferekides, D. Marinskiy, V. Viswanathan, B. Tetali, V. Palekis, P. Selvaraj, D.L. Morel, Thin Solid Films 361-362 (2000) 520.
[4] T. Moriga, Y. Hayashi, K. Kondo, Y. Nishimura, K. Murai, I. Nakabayashi, J. Vac. Sci. Technol. A 22 (4) (2004) 1705.
[5] R. Mamazza, U. Balasabramanian, S. Gayam, S. Bapanapalli, L. Nemani, M. Jayabal, H. Zhao, D. Morel, C.S. Ferekides, Proceedings of 31st IEEE Photovoltaic Specialist Conference, 2005, p. 283.