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Transparent high-performance CDSE thin-film solar cells

P. Mahawela, S. Jeedigunta, S. Vakkalanka, C.S. Ferekides*, D.L. Morel

Department of Electrical Engineering, Clean Energy Research Center, University of South Florida, 4202 E. Flower Ave., 33620 Tampa, FL, USA

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Abstract

Simulations indicate that 25–30% efficiency can be achieved with a four-terminal thin-film tandem structure. The bottom low band gap cell can be $CuIn_{1-x}Ga_xSe_2$, and CdSe is proposed as the top cell, as it has an ideal band gap of 1.7 eV. In addition to the efficiency requirements, the top cell must also be transparent to effectively transmit sub band gap light to the bottom cell. We have developed CdSe devices that meet many of the requirements of this tandem structure. High electronic quality CdSe has been deposited on SnO_2 and ZnO, which serve as the transparent n-type contact. The p-type transparent contact is ZnSe/Cu. Voc's of 475 mV have been achieved and can be further improved with better contacts. However, record Jsc's in excess of 17 mA/cm^2 have been achieved. This is close to the target 18 mA/cm^2 to meet the efficiency objectives. Transmission of 80% of the sub band gap radiation has been demonstrated for 2-μm-thick absorber layers. This is also close to the 85% target to achieve the overall tandem efficiency objectives. Improvement of the contact layers to achieve the Voc target is the final challenge.

Keywords: CDSE; Thin film; Solar cells

1. Background

Compound semiconductor thin film solar cells are approaching 20% efficiency. Through the development of tandem thin film structures, it is possible to achieve efficiencies in the 25–30% range [1]. $CuIn_{1-x}Ga_xSe_2$ (CIGS) with a band gap of 1.0 eV is an ideal choice for the low gap cell. The top cell should have a band gap in the range 1.6–1.9 eV. $Cd_{1-x}Zn_xTe$ can be tuned to this range and has been under development for this purpose [2]. CdSe has an ideal band gap of 1.7 eV, has shown potential as a single junction device over a long period of time [3], and, recently, we presented results on the first transparent CdSe devices that were specifically designed for tandem applications [4]. In this paper, we report the results of our efforts to develop transparent CdSe devices that can be used in tandem four-terminal structures.

2. Experimental

The standard substrate used for all the devices is a transparent conductor (TC), such as tin oxide (TO) or ZnO, on a Corning 7059 glass. TO is deposited by chemical vapor deposition (CVD) at 500 °C and is doped with fluorine. ZnO is sputtered from a ZnO target containing an Al dopant. The sheet resistivity of the transparent conductor (TC) layer is typically in the range 10–50 Ω/□. The CdSe absorber layer is deposited by physical vapor deposition from a CdSe source at a substrate temperature of about 580 °C. Absorber layer thickness is in the range 1–2 μm. ZnSe and ZnTe have been used as the p-contact. They are deposited by physical vapor deposition from a compound source at substrate temperatures from 25 to 200 °C. Typical layer thickness is 20 nm. Finally, a Cu or Au layer of thickness 2–10 nm is deposited on the ZnSe or ZnTe. The entire p-contact layer is deposited through a shadow mask that results in an array of devices of area 0.1 cm^2.

Film characterization involves the routine use of energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray

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

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diffraction (XRD). Device characterization includes light and dark current-voltage (IV) dependence, quantum efficiency (QE) response, and capacitance-voltage (CV).

3. Results and discussion

3.1. Absorber properties

Significant progress has been made with demonstrating high-electronic-quality CdSe on transparent contacts. The device format is the glass/TC/CdSe/ZnSe/Cu structure shown in Fig. 1. Typical layer thicknesses are the following: CdSe, 2 μm; ZnSe, 20 nm; Cu, 2–10 nm. In this structure, both contacts are transparent. As discussed above, TC refers to either tin oxide (TO) or ZnO, and this is the n-contact that has a work function close to the CdSe conduction band edge. As shown, its conduction band should align with that of CdSe to avoid the formation of an unfavorable barrier to electron flow. ZnSe is the p-contact and is also "transparent" by virtue of its 2.6 eV band gap. Ideally, its valence band should align with that of CdSe, and its Fermi level should be close to the valence band edge of CdSe. The parameters for TO, ZnO, and ZnSe are close to what is needed for these contacts, and the alignments in Fig. 1 are based upon actual layer properties.

Device performance is significantly higher for light incident from the ZnSe/Cu side because the CdSe is much thicker than our ultimate targeted thickness of 0.2–0.8 μm. This is also consistent with CdSe's inclination to be n-type. For devices in our targeted thickness range, this should not matter, since we expect complete depletion, as indicated in Fig. 1. Under such conditions, in principle, light could be incident from either side. In practice, this would be feasible only if the transport properties are suitably high for both carriers. Notwithstanding the 2-μm CdSe layer thickness, the much lower output for light incident from the n-contact side that we are observing suggests that hole transport is somewhat inferior to electron transport.

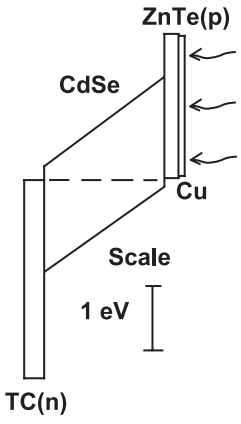

Fig. 1. Schematic band diagram of proposed TC/CdSe/ZnSe/Cu solar cell.

Much of the early work on thin-film CdSe employed Cr as the growth surface [2]. Some preference for (0 0 2) orientation was observed, although this was affected by growth conditions [2]. The best film performance was also thought to be associated with preferred orientation. In Fig. 2, we show an XRD spectrum of a typical film grown on SnO_2. As can be seen, the strongest peak is (1 0 3), but there is no preferred orientation, and (0 0 2) is fairly subdued. We have not yet determined a dependence of film performance on orientation, but as will be discussed below, we have achieved excellent electronic properties with the mixed orientation exhibited in Fig. 2.

3.2. p-Contact properties

One of the most difficult aspects of this effort is the p-contact. It is commonly known that p-contacts to II-VI materials are difficult to develop. This has, in fact, been one of the limitations in advancing CdTe solar cells, and there is currently a substantial effort to develop new options. The current most successful back contact is a somewhat ill-defined graphite paste containing Cu and Hg. Compounding the problem here is the fact that the contact has to be transparent. Unfortunately, most transparent conductors are n-type. However, there are recent reports of p-type ZnO [5]. ZnO's valence band is about 0.8 eV below that of CdSe, hence, some type of tunneling contact would have to be developed. If so, one might expect ZnO to be both the n- and p-contact.

Another approach is to use a p-contact that is not a degenerate transparent conductor. ZnSe is an ideal choice in terms of its large band gap and favorable valence band alignment with CdSe. However, it is normally highly resistive. Nevertheless, doping levels in the 10^{18}–$10^{19}/cm^3$ range using Na and N doping have been reported [6,7]. This should place the Fermi level close to the valence band, as desired, and with the higher levels, it is possible to also think of tunneling contact. Unfortunately, these results are from ideal growth conditions using MBE, and this type of deposition process is not suitable for a solar cell production line. We are thus devoting considerable effort to the development of transparent p-contacts with the requisite properties using acceptable deposition processes. Results of our efforts to dope ZnSe will be reported in future publications. The focus of this paper is the development of the absorber layer, and our standard ZnSe contact is adequate to proceed. While the as-deposited ZnSe is highly resistive, the deposition of the thin Cu layer on the ZnSe changes its properties significantly. In fact, the Cu layer diffuses with time into the ZnSe layer, and some Cu may diffuse into the CdSe layer as well. Until this occurs, device output is not optimal. Cu is known to diffuse in most host materials, and that is no less the case here. We expect that some doping occurs, and the ZnSe layer is more properly written as ZnSe/Cu.

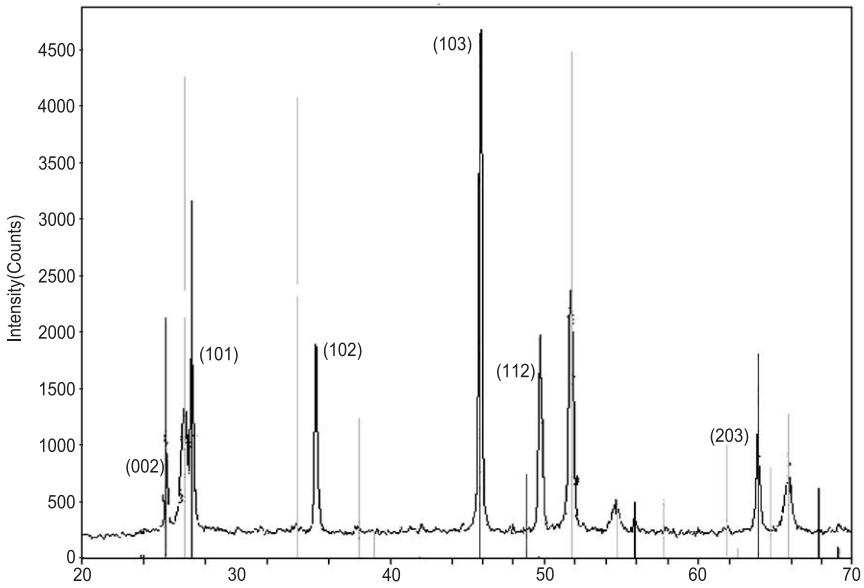

Fig. 2. XRD spectrum of CdSe deposited at 580 °C on Corning 7059 glass coated with tin oxide.

Before proceeding to the electronic properties, as manifested in device performance, we first consider the optical aspect of this contact. In Fig. 3, we show a breakdown of the transmission spectra for the layers on glass. In this case, the layer thicknesses are 20 nm for ZnSe and 6 nm for Cu. There are several factors to consider in utilizing these results. First, the properties of ZnSe/Cu deposited on glass are not quite the same as those deposited on CdSe. Second, there is evidence that Cu is reacting with ZnSe. The degree of reaction is expected to be a function of the ZnSe properties, hence, the resulting transmission of the ZnSe/Cu stack has to be tracked as we vary those conditions. Nevertheless, as seen in Fig. 3, most of the transmission loss is attributable to the Cu. At some thickness of Cu, adding additional Cu will result in a straightforward reduction in transmission. We have not yet taken the data for this determination because the integrity of the ZnSe is still an issue. XRD analysis indicates that the ZnSe that we have used thus far seems to be amorphous, with a small amount of crystallinity. As we vary the deposition conditions, we see changes in structure and in the absorption profile. While the transmission profile of Fig. 3 is representative, additional analysis is necessary to determine the amount of light reaching the absorber. Previously, we reported a record 14.7 mA/cm^2 external Jsc and, through such analysis, an internal Jsc of 18.3 mA/cm^2[4]. A Jsc of 18 mA/cm^2 is what is needed to attain the performance objectives. This then indicated that the CdSe absorber had the potential to meet the current density objective. As will be discussed below, our recent results validate this assertion.

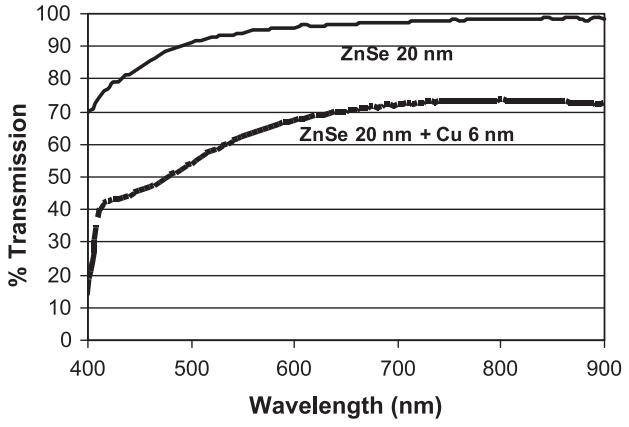

Fig. 3. Transmission spectra for 20 nm of ZnSe on glass and 20 nm of ZnSe plus 6 nm of Cu on glass.

3.3. Device performance

In Fig. 4, we show the dark and light IV curves for a typical device with a ZnSe/Cu p-contact. As can be seen, the

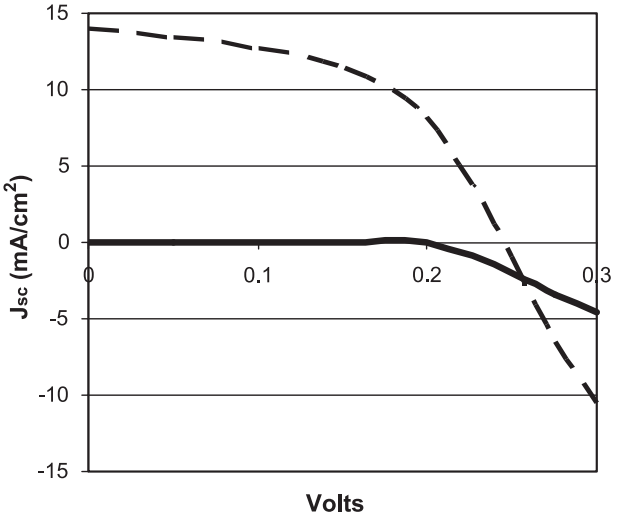

Fig. 4. Representative light and dark IV curves for glass/TO/CdSe/ZnSe/Cu devices. Light incidence is from the ZnSe/Cu side.

power curve is fairly normal; however, there is significant crossover, i.e., lack of superposition. This is commonly observed in many thin-film solar cells, and its cause depends upon the details of device structure. In this case, the slow turn-on of the dark curve is thought to be due to a light-sensitive resistance.

To achieve efficiency in the 16–18% range, the Voc needs to be about 1 V. The 250 mV seen in Fig. 4 is far below this value. By varying the properties of the contacts while keeping the absorber properties constant, we have determined that the low Voc is due to both contacts, primarily the p-contact. Through these preliminary efforts with the contacts, we have reached Voc's approaching 500 mV. However, our focus here is on the integrity of the absorber, and to first order, Voc's in this range are not an issue for that purpose. Subsequent to the Jsc results presented above, we have been improving the optical properties of the p-contact and have made some progress in that direction. However, it seems that the nature of the bottom contact plays a role as well. In growing our CdSe layers on NREL-supplied TO, we realized a substantial increase in Jsc. In Fig. 5, we show QE spectra for three devices with Jsc in excess of 17 mA/cm^2. Jsc is determined by integrating the QE spectrum using NREL-calibrated reference cells. The spectral breakdown of the record currents is shown in Table 1. This result suggests that the growth surface strongly influences resulting film properties. And most important, the result verifies the high electronic quality of the absorber and its ability to meet the performance objectives. Having achieved this level of performance with CdSe, we have turned our attention to the further development of the contacts to improve Voc.

3.4. Optical considerations

Although one might well consider an efficient single junction CdSe cell as an end in itself, it would have to compete with CdTe in that regard, which has a more ideal band gap of 1.45 eV. As the top of a tandem structure, however, its higher band gap is an advantage and justifies the effort for its development. We have proposed a four-terminal tandem because it decouples the fabrication and operation of the component cells. However, an added requirement of a four-terminal structure is to couple sub band gap light effectively to the underlying cell. We have conducted AMPS© simulations using known properties of the cell components and have determined that an absorber in the thickness range 600–800 nm is optimum [1]. This thickness is sufficient to absorb the high energy light and makes complete depletion easier to achieve. As indicated above, our typical device thickness is about 2 μm. CV measurements indicate near depletion, and as seen in Fig. 6, even with this excessive thickness, we achieve good transmission of sub band gap light. In our simulations, we used 85% transmission to simulate an achievable efficiency level of 25% for the tandem structure [1]. The 80% level demonstrated in Fig. 6 with a 2-μm-thick film instills great confidence that the 85% level will be achieved when we reduce the absorber thickness to the design range. Thus, we have basically achieved the requisite properties for the absorber in our transparent top cell. The remaining challenge is to advance the Voc from 475 mV to the 1 V level, and we are working deliberately on that objective.

Table 1
Spectral distribution for Jsc for three glass/TO/CdSe/Cu devices exhibiting total Jsc in excess of 17 mA/cm^2

	Device		1	2	3
	From (nm)	To (nm)	Jsc	Jsc	Jsc
Region 1	300	400	0.10	0.10	0.10
Region 2	400	510	4.59	4.52	4.42
Region 3	510	650	8.76	8.59	8.56
Region 4	650	800	3.95	3.89	3.98
Region 5	800	900	0.02	0.02	0.02
Total Jsc(mA/cm^2)			17.43	17.13	17.08

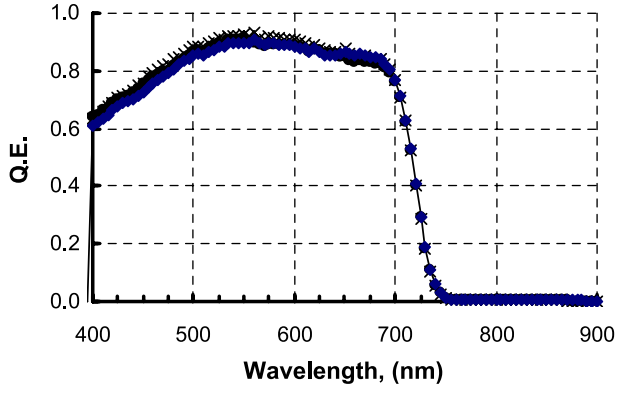

Fig. 5. QE spectra for three glass/TO/CdSe/ZnSe/Cu devices exhibiting Jsc in excess of 17 mA/cm^2.

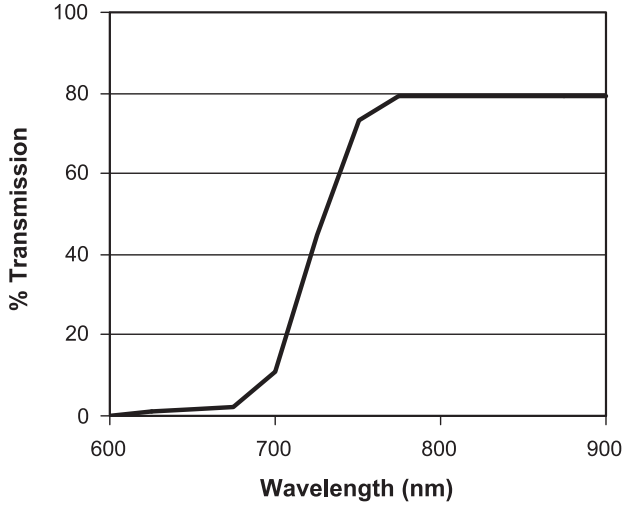

Fig. 6. Transmission spectrum for 2-μm-thick CdSe on TC/glass.

4. Conclusions

In earlier publications, we presented the results of simulations that defined performance objectives needed to attain 25% efficiency in a II-VI-based thin-film four-terminal tandem cell. In this paper, we addressed those objectives for the top high band gap cell using CdSe as the absorber. A key aspect of the device design is that it must be transparent to effectively transmit sub band gap light to an underlying low band gap cell such as CIGS. We demonstrated that high-electronic-quality CdSe could be grown on a transparent conductor such as TO and ZnO, which also serves as the n-contact. The current p-layer contact is ZnSe/Cu. It was proposed that some of the deposited Cu doped the ZnSe, and the combination of ZnSe/Cu with residual Cu produced an effective p-contact. The optical properties of this layer are a function of the deposition conditions and can be dominated by those of ZnSe in films, where Cu is adequately dispersed. Although this contact is adequate to evaluate the CdSe absorber, Voc's are currently below 500 mV because the effective contact energy is still not low enough in the band gap. Efforts are underway to increase doping levels that should result in higher Voc.

Several devices were fabricated with Jsc's in excess of 17 mA/cm^2, which is a record for thin-film CdSe, especially in a transparent structure. This demonstrates the high electronic quality of the CdSe absorber and is close to the value of 18 mA/cm^2 needed to meet the 25% tandem objective. Another targeted objective is to transmit 85% of the sub band gap radiation to the bottom cell. We presented data demonstrating 80% transmission for a 2-μm-thick CdSe layer. As we thin this to the target range of 800–1200 nm, we are confident that this second objective can be met. The key to the achievement of the efficiency objective for the transparent CdSe cell is higher Voc's. We are currently working on improving the properties of both contacts to accomplish this last requirement.

Acknowledgments

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