Band alignment of front contact layers for high-efficiency CdTe solar cells

J.M. Kephart^a, J.W. McCamy^b, Z. Ma^b, A. Ganjoo^b, F.M. Alamgir^c, W.S. Sampath^a

^aDepartment of Mechanical Engineering, Colorado State University, 1320 Campus Delivery, Fort Collins, Colorado 80501 USA

^bPPG Industries, Inc., 400 Guys Run Road, Cheswick, Pennsylvania 15024 USA

^cSchool of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, N.W., Atlanta, Georgia 30332-0245 USA

Abstract

Resistive oxide materials play an important role in the front contact of CdTe solar cells. The high-resistance transparent (HRT) or “buffer” layer has been used extensively in CdTe thin-film photovoltaics to enable a reduction in CdS thickness while maintaining near-maximum device voltage and fill factor. SnO₂- and ZnO-based alloys were tested as HRT layers on a fluorine-doped tin oxide transparent conducting oxide. SnO₂-based alloy HRT layers were deposited via atmospheric pressure chemical vapor deposition (APCVD). Alloying ZnO with MgO to create Mg_xZn_{1-x}O (MZO) via radio-frequency sputter deposition was explored as a way to reduce the electron affinity of ZnO HRT layers. To fully understand the behavior of these materials, many devices were fabricated with either no CdS layer, a sublimated CdS layer, or a sputtered, oxygenated CdS layer. MZO layers resulted in high open-circuit voltage and device efficiency even with the complete elimination of the CdS layer. In both HRT systems, controlling electron affinity to optimize front contact band alignment is an important consideration. Band measurements using photoelectron spectroscopy and synchrotron techniques correlate band alignment measurements with efficiency parameters in the design of HRT and CdS layers.

Keywords: thin-film photovoltaics, radio frequency sputter deposition, transparent conducting oxides, UV photoelectron spectroscopy, II-VI semiconductors

1. Introduction

Cadmium telluride thin-film solar cells have recently seen a rapid increase in record cell efficiency to 21.5% [1]. Part of this increase is due to the high optical collection of this technology [2]. Typically, CdTe thin-film solar cells are grown in the superstrate configuration, using glass coated with a trans-

parent conducting oxide (TCO). Another oxide layer, dubbed the high-resistance transparent (HRT) or “buffer” layer, is often deposited on the TCO. “High-resistance” does not necessarily mean insulating but orders of magnitude more resistive than the TCO. Typically, a CdS-based layer is deposited on the HRT. CdS is a strong absorber of light with energy above

its bandgap of 2.4 eV, and light absorbed in this layer is wasted because carriers photogenerated in the CdS are not collected. When the CdS layer is too thin the operating voltage of the cell degrades, so the CdS thickness that optimizes efficiency must balance current and voltage at the maximum power point.

Empirically, the presence of an HRT layer has been shown to lessen the degradation in voltage as the CdS thickness is decreased, allowing a thinner CdS layer and higher optimum efficiency. While the resistance of the layer plays a role in its effect, not all resistive oxides are effective HRT layers, and other electronic properties must also be considered. A recent review by Klein explains the science of interface band alignment in chalcogenide semiconductors and discusses the CdS/CdTe interface as well as different oxides used as HRT layers [3]. In previous work by the authors, a highly transparent oxygenated CdS layer was shown to be compatible with one SnO₂-based HRT and the importance of band alignment for the oxygenated CdS layer was shown [4]. Here, a combination of numerous device results, modeling, and band measurements show the importance of band alignment using HRT layers within the zinc oxide and tin oxide systems. Cells are demonstrated using oxide layers that allow for high efficiency with the elimination of the CdS layer.

The most commonly used TCO in commercial CdTe cells is fluorine-doped SnO₂ (FTO) because it can be deposited during the glass manufacturing process with high throughput and is mostly inert to

subsequent processing steps. Still, cells have successfully been made using In₂O₃:Sn [5], Cd₂SnO₄ [6], and ZnO:Al [7]. Many TCO/HRT combinations have been studied, with HRT layers including ZnO [8], In₂O₃ [9, 10], Ga₂O₃ [9], SnO₂ [11, 9, 10, 12], and alloys of these materials such as zinc stannate [13, 14]. A universally described feature of these layers is their increased resistivity relative to the TCO.

One hypothesis of the HRT's role in CdTe solar cells considers the effect of pinholes, or small areas where there is no CdS coverage, and through which CdTe directly contacts the oxide layer. According to this explanation, a diode with maximum open-circuit voltage and fill factor will be formed regardless of layer thickness as long as there are no CdS pinholes. The pinhole area that contacts the oxide below is a weaker diode with high forward current and low open-circuit voltage [9]. A loss in open-circuit voltage occurs when CdS thickness is reduced, and this is ascribed to an increasing fractional pinhole area the substrate [12]. This theory assumes that pinhole area increases as overall CdS layer thickness decreases. By adding an ohmic resistor between the TCO and the CdS, the theory states, less CdS is required because the shunting effect of the pinhole area is reduced.

In devices made at Colorado State University there is no evidence that the existence of pinholes is correlated with CdS layer thickness [15]. Electron microscopy has shown that films 20-30 nm thick have coalesced grains without exposing the TCO. Thick-

nesses of close to 100 nm of this CdS material are needed to obtain maximum open-circuit voltage. Statistical measurements have not shown an increase in pinhole area with reduced CdS thickness for films made at CSU. Devices that have both lower pinhole area and reduced CdS thickness nevertheless show lower V_{OC} relative to a control, indicating that CdS layer thickness is an important variable independent of pinholes [16]. Overall, the role of the HRT has not been considered clear or fully understood with yet another possibility involving the effects of thermal expansion [17]. Further understanding of which material properties affect HRT function is needed to find more ideal contacts which allow the most light possible to reach the absorber. Here, band alignment of the front contact layers, which is known to be important but seldom discussed in this context, is investigated as a key concept to complement the existing understanding.

2. Material and Methods

All devices reported in this work fall within the following structure: the glass is 3.2-mm soda-lime glass, the TCO is fluorine-doped tin oxide, the HRT is either absent, SnO_2 -based, or ZnO -based, and the CdS layer is either absent, sputtered oxygenated CdS, or sublimated CdS. Commercial low-iron soda-lime glass coated with $10\text{-}\Omega/\square$ $\text{SnO}_2\text{:F}$ TCO (“R10H1” manufactured by PPG Industries, Inc.) was the baseline substrate for the SnO_2 -based HRT layers studied here. SnO_2 -based HRT layers were deposited

on FTO using atmospheric pressure chemical vapor deposition (APCVD) in a laboratory reactor, which simulates the in-line manufacturing process. All SnO_2 -based HRT layers deposited by PPG Industries had tin as a minimum of 80 at% of cations. Radio-frequency sputter-deposited ZnO -based layers were deposited on TEC 10 (manufactured by Nippon Sheet Glass Co., Ltd.), a similar FTO-coated soda-lime glass product. For these layers a 10-cm diameter target was used with a power of 180 W, frequency of 13.56 MHz, a pressure of 5 mTorr, 1% O_2 in argon, and a target-substrate distance of 15 cm. Targets were 99.99% pure, hot-pressed, mixed-powder targets (Plasmaterials, Inc.) with a 99.999% pure ZnO target (Kurt J. Lesker) used for comparison.

Complete thin-film CdTe solar cells were prepared in the CSU Advanced Research Deposition System (ARDS). This system was used for sublimated CdS, CdTe, CdCl_2 and Cu process steps. Cell fabrication and oxygenated CdS procedures have been described in detail [4]. Solar cell efficiency measurements were performed using a xenon arc lamp with AM1.5 filter; short-circuit current density was calibrated to cells measured by NREL.

Band measurements were performed using a PHI 5800 X-ray Photoelectron Spectroscopy system with a PREVAC UVS40A2 UV source. Samples were cleaned and heated in the ARDS to approximate the condition of the surface prior to semiconductor deposition, removed from the ARDS under an inert environment, and prepared in a glovebox under argon.

Air exposure of the samples was less than 10 seconds during loading into the XPS system to limit atmospheric contamination of the surface. Measurements had a take-off angle of 85° and a sample bias of -5 V. Analysis followed the procedure of Helander *et al.* [18]. Synchrotron-based measurements were performed on beamline X1B at the National Synchrotron Light Source at Brookhaven National Laboratory. A beam energy of 550 eV was used for XES which corresponds to an attenuation length in SnO_2 of 80 nm [19]. A range of approximately 522-554 eV was scanned to obtain the O-K-edge XAS.

3. Results

3.1. SnO_2 -based HRT layers

Many candidate SnO_2 -based HRT layers were tested in devices with various alloying elements, alloy compositions, and thicknesses. Alloying elements tested were Zn, Ga, In, and N as well as un-alloyed tin oxide in the thickness range of 80-250 nm. These layers were screened to test quickly which were most effective. A preliminary experiment was devised with one substrate each of thick (> 120 nm) and thin (< 90 nm) sublimated CdS using both the TCO/HRT/CdS/CdTe and TCO/CdS/CdTe structures. The difference between voltage and fill factor of these devices with and without HRT was statistically tested to determine if an HRT effect was significant. The best-performing SnO_2 -based HRT layer was found to be a dilute (2-3 at%) zinc-doped tin oxide using monobutyl tin trichloride and diethyl zinc as precur-

sors; an HRT thickness of 150 nm was found to be optimal. This HRT layer was used in subsequent experiments in which the sublimated CdS layer thickness was varied.

Devices with the structure TCO/HRT/sublimated CdS/CdTe were made using the $\text{SnO}_2\text{:Zn}$ HRT, and devices with the structure TCO/sublimated CdS/CdTe served as a control (see Figure 1). Device quality had little dependence on CdS layer thickness above a critical value of about 90 nm for devices without HRT and 60 nm for devices with HRT. Below this value, V_{OC} gradually declined with a minimum at 0 nm (a device with no CdS layer). Meanwhile, current continuously improved with thinner CdS. Devices with the HRT showed both a lower critical thickness and a higher V_{OC} with 0 nm of CdS. For all values of CdS thickness, devices typically exhibited high shunt resistance. The best devices with the structures TCO/CdTe, TCO/HRT/CdTe, TCO/CdS/CdTe, and TCO/HRT/CdS/CdTe are shown in Figure 2. With a CdS layer, the increased current with HRT was a greater effect than the slightly reduced voltage, highlighting the importance of short-circuit current gains as the benefit of the HRT layer.

CdTe devices often show light-dark crossover that increases as CdS thickness decreases. Some devices with the structure TCO/CdTe (without any HRT or CdS layer) exhibit strong light-dark crossover, in which even low illumination levels cause a large drop in series resistance compared to the dark measurement. This behavior was examined by illuminating the de-

vices with red and blue light-emitting diodes and varying the supply current by several orders of magnitude; both the LED current and the short-circuit current were measured, and remained linearly related over the measurement range. Figure 3a illustrates the drastic change in series resistance as LED intensity is varied over several orders of magnitude, corresponding with a change in photocurrent. Figure 3b illustrates this phenomenon in parametric form for both blue and red LED illumination. The relationship between J_{SC} and series resistance for this device is comparable when red and blue LEDs are used. The presence of light greatly reduces the barrier to forward electron current. This change is opposite in direction and much larger in magnitude than the photocurrent, indicating that low levels of photogenerated carriers can modify the junction behavior. For devices that do have CdS, this light-dark crossover can be due to photoconductivity in the CdS, which occurs when blue light is present [20]. Here, no CdS layer is present, and the series resistance of the diode in forward bias is a function of the light absorbed in the CdTe regardless of whether red or blue light is used. Therefore, the light appears to be filling charged states at the TCO/CdTe interface rather than in any CdS layer. Negatively charged interface defects have a similar band alignment effect as a contacting material with high electron affinity, and these two properties have additive effects. For a variety of front contacts, higher V_{OC} is correlated with reduced light-dark crossover.

3.2. ZnO-based HRT layers

ZnO has been used as an effective HRT. When CdTe is deposited directly on sputtered ZnO, V_{OC} of 500-600 mV or more is produced. Band alignment measurements by Rao *et al.* indicate that ZnO has a larger electron affinity than CdS; alloying with MgO to produce $Mg_xZn_{1-x}O$ (MZO) with a composition of $x = 0.15$ can reduce the electron affinity and produce a flatter conduction band alignment with CdS [21]. In Cu(In,Ga)Se₂ thin-film solar cells, this alloy has been shown to have superior performance as a replacement for ZnO in the front contact [22]. $Mg_xZn_{1-x}O$ has the added benefit of increasing the optical bandgap of the layer for better ultraviolet light transmission [23]. Varying the magnesium content from $x = 0$ to $x = 0.30$ allowed Erfurth *et al.* to tune the conduction band offset (CBO) between a “cliff,” or negative CBO, and a “spike,” or positive CBO, with both open-circuit voltage and fill factor improving with magnesium addition [24].

Over the range $x = 0$ to $x = 0.24$, the films remain in the wurtzite crystal structure with the lattice constant c reducing from 0.5211 nm to 0.5155 nm for films deposited on glass at 300 °C [25]; the lattice constant c for wurtzite CdS is 0.6756 nm. This trend also extends to the lattice constant a in the close-packing direction, which is more relevant for CdTe growth. The constant a is smaller for CdS than for CdTe, so further decreasing this parameter would increase lattice mismatch. If lattice mismatch with CdTe were a decisive factor in the quality of this polycrys-

talline interface, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ would produce diodes with the poorest performance.

In this work $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ was examined in devices with no CdS layer in the structure TCO/ $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ /CdTe, deposited by RF sputter deposition using target compositions of $x = 0.15, 0.20$, and 0.25 (MgO weight percentages of 8, 11, and 14% with the remainder ZnO). Pure ZnO was also tested as a comparison. Films made from these targets exhibited the expected increase in optical bandgap relative to ZnO; measurements by XPS of the film made from the 11 wt% target show the magnesium content is slightly higher in the film ($x = 0.23$) than in the target ($x = 0.20$) in agreement with Hariskos *et al.* [22]. At each composition, a thicker film with measured thickness near 500 nm was deposited on uncoated glass for optical measurements. In Figure 4 the transmission is shown over a wide wavelength range along with the optical bandgap calculated from Tauc plots of the data. The films are transparent from their bandgap in the range of 350-400 nm out to long wavelengths up to $2\text{ }\mu\text{m}$. The Tauc plot shows that bandgap increases, as expected, with increasing magnesium composition.

$\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films approximately $1\text{ }\mu\text{m}$ thick at each magnesium concentration were deposited on low alkali Eagle XG glass (Corning Inc.) in order to limit the potential electronic effects of sodium diffusion. Small, 1-cm square samples were prepared with soldered indium contacts as corner electrodes, and Hall measurements were attempted using an Ecopia HMS

3000 using the van der Pauw method. The samples were too resistive to measure, implying a resistivity of $10^7\text{ }\Omega\text{-cm}$ or greater. The resistivity of the film when deposited on a TCO layer would additionally depend on the band alignment in the structure.

Layers from 25-400 nm thick were deposited on FTO-coated glass and devices were subsequently fabricated, using no CdS layer (shown in Figure 5). The device with a ZnO layer has low V_{OC} which is attributed to a flat or slightly negative CBO in combination with interface defects. The 8 wt% sample has high V_{OC} and fill factor. Almost all the devices with thickness above 50 nm show excellent V_{OC} near 850 mV; however, thinner layers show reduced V_{OC} , an effect that becomes stronger with lower magnesium content. The $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ layers with higher magnesium exhibit a strong secondary barrier in the J-V curve with 100 nm or greater thickness. At the optimal point of 50 nm, made with the 11 wt% MgO target, numerous devices with efficiency values of over 15% have been fabricated with no CdS-based layer, and no antireflection layer. This demonstrates use of a thin, resistive oxide layer which replaces both as HRT and CdS layers when composition and thickness of the layer are preliminarily optimized. The J-V curves of devices with 100-nm thick $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ layers of each composition are shown in Figure 6. The 11 wt% and 14 wt% samples have high V_{OC} and a secondary barrier (kink) in the J-V curve, attributed to a positive CBO. The 11 wt% has a larger kink, which is likely due to process variability; in

general, small changes in J-V behavior are observed with target break-in. There is a clear interaction between thickness and composition in determining V_{OC} and barrier behavior that can be used to reach an optimum.

In the context of CdTe devices there are many similarities between $Mg_xZn_{1-x}O$, and sputtered, oxygenated CdS that was explored in previous work [4]. Relative to sublimated CdS, oxygenated CdS has a lower carrier concentration, and can be tuned to have a larger bandgap and lower electron affinity. Like oxygenated CdS, $Mg_xZn_{1-x}O$ also has a very low carrier concentration. Relative to ZnO, $Mg_xZn_{1-x}O$ has a higher bandgap and lower electron affinity. In devices, an increase in oxygen content in oxygenated CdS can produce higher current and voltage, but causes a secondary barrier (kink) to appear. $Mg_xZn_{1-x}O$ layers that are thicker and contain more Mg also tend to exhibit higher secondary barriers in devices. This phenomenon has been previously explained by 1-dimensional device modeling in which the electron affinity of the CdS layer was decreased and a secondary barrier was produced.

3.3. Band Measurements of HRT layers

A subset of all the SnO_2 -based HRT layers tested were chosen with a variety of alloying element and concentration, with a standard thickness of 150 nm if available. The ZnO and 11 wt% $Mg_xZn_{1-x}O$ were also measured using the best-performing thickness of 50 nm deposited on TEC 10. Three sets of devices and band measurements were made with this set of

HRT layers. The first set was made without any CdS layer. A second set of devices was made with a 50 nm oxygenated CdS layer, and a third set used 50 nm sublimated CdS. The selected subset of HRT layers was measured by UPS. These measurements are summarized in Table 1. The work function and Fermi level were measured, and electron affinity was calculated as a way to estimate band alignment. For each combination of parameters, a substrate with nine devices was prepared with a device area of 0.7 cm^2 . The sputtered, oxygenated CdS has very low free-electron concentration which was measured at approximately 10^{12} cm^{-3} using Hall measurements after annealing to process temperatures of 500°C . Figure 7a shows that for devices without CdS, electron affinity is a strong predictor of V_{OC} (as well as efficiency). For devices with 50 nm of oxygenated CdS in between the HRT and CdTe (Figure 7b), the dependence becomes weaker. The dependence is weaker still for devices with sublimated CdS (Figure 7c).

The fluorine-doped tin oxide TCO and optimal $SnO_2:Zn$ HRT were characterized via x-ray emission spectroscopy and x-ray absorption spectroscopy at a photon energy of 550 eV using a synchrotron beamline. These techniques do not require emission of a photoelectron and therefore probe more deeply than XPS and UPS, with an attenuation length of approximately 80 nm. This makes the measurements insensitive to surface contamination which is typically less than 1 nm but can strongly affect surface-sensitive band measurements for some materials. This sup-

ports photoelectron spectroscopy band measurements³⁸⁵ and indicates they are not due to an interaction with³⁸⁶ adventitious materials. X-ray absorption spectroscopy³⁸⁷ probes the unoccupied states of the material; the ground-³⁸⁸ing current of the sample is measured to determine³⁸⁹ the extent of absorption. X-ray emission spectroscopy³⁹⁰ measures the energy of X-rays that are emitted when³⁹¹ electrons fall from valence states to core holes cre-³⁹²ated by incident radiation. These techniques show³⁹³ that both the valence and conduction bands shift away³⁹⁴ from core states in the HRT versus the TCO, indicat-³⁹⁵ing that the HRT has a lower electron affinity, as seen³⁹⁶ in Figure 8.

3.4. 1-D modeling of HRT layer band alignment

Modeling of 1-dimensional structures was con-³⁹⁹ducted in the SCAPS software [26]. This model is a⁴⁰⁰ simplification of the actual cell and ignores phenom-⁴⁰¹ena related to polycrystallinity. Some properties of⁴⁰² the baseline cell are shown in Table 2; parameters not⁴⁰³ directly related to the front contact were mostly taken⁴⁰⁴ from Ref. [27] and other parameters were varied to⁴⁰⁵ perform the study. The absorber lifetimes were set⁴⁰⁶ to 2 ns for both holes and electrons. The layer thick-⁴⁰⁷ness values were set to match experimental samples.⁴⁰⁸ The first set of models explores the effect of HRT⁴⁰⁹ electron affinity when no CdS is present. The light⁴¹⁰ dependence of the TCO/CdTe diodes with no CdS as⁴¹¹ shown in Figure 3 implies the presence of charged⁴¹² defects at the CdTe/oxide interface. The oxide/CdTe⁴¹³ interfaces are also likely to have high surface recom-⁴¹⁴bination velocity due to poor lattice matching. To⁴¹⁵

model these effects, acceptor-like interface defects⁴¹⁶ were placed at the SnO₂/CdTe interface in the middle⁴¹⁷ of the CdTe bandgap with a density of $2 \cdot 10^{12} \text{ cm}^{-2}$,⁴¹⁸ and interface recombination velocity was set to 10^7 ⁴¹⁹ cm/s.

The experimental results for devices with no CdS⁴²⁰ suggest that a higher electron affinity should result in⁴²¹ a reduced open-circuit voltage of the cell. The ef-⁴²²fect of the modeled band structure on model J-V be-⁴²³havior can be seen in Figure 9. The results in figure⁴²⁴ 9b correspond with the curves in Figure 6 and 7a.⁴²⁵ Varying the oxide electron affinity in the model pro-⁴²⁶duces a similar variation in J-V characteristics. As⁴²⁷ the CBO becomes flat or a cliff, there is both a de-⁴²⁸creasing device voltage and fill factor and an increas-⁴²⁹ing loss of current due to interface recombination. In⁴³⁰ real devices, this loss would depend not only on band⁴³¹ alignment but the defect concentration and carrier⁴³² concentration for the specific oxide. When the elec-⁴³³tron affinity of the oxide is reduced to 4.0 eV, a kink⁴³⁴ appears in the current density-voltage curve, as with⁴³⁵ high-magnesium MZO layers in Figure 6. Based on⁴³⁶ the band alignment measurements, SnO₂-based ox-⁴³⁷ides have band alignments from flat to a 0.9 eV cliff.⁴³⁸ For ZnO-based HRT layers, the ZnO appears to have⁴³⁹ a nearly flat conduction band offset. The optimized⁴⁴⁰ MZO layer has a spike in the conduction band of⁴⁴¹ about 0.3 eV at the interface. Experimental V_{OC} re-⁴⁴²sults from Figure 7 are compared to model results in⁴⁴³ Figure 10a.

When 50 nm of CdS or oxygenated CdS is present,

the lowest experimental open-circuit voltages are approximately 600 mV, and the slope of the lines in Figure 7b and c is reduced. A large barrier to electron injection would be expected at the oxide/CdS interface for oxides with high electron affinity, but this is not seen in actual devices; the oxide/CdS interface is also likely much different than the various oxide/CdTe interfaces. The band alignment of this interface is pinned in a relatively narrow range due to defects in CdS as discussed by Klein [3]. A 50 nm layer of CdS was added to the model to form an oxide/CdS/CdTe structure. This CdS layer has donor-like defects placed 0.5 eV below the conduction band minimum. Figure 10b compares experimental and model V_{OC} results with modeled CdS. With the CdS layer present, the device parameters are insensitive to small negative or positive CBO's. As electron affinity is increased above 4.6 eV, the device voltage is reduced. For larger oxide electron affinities a barrier appears in the model J-V curves that is never observed in experimental devices with CdS; also, if the oxide electron affinity is 4.0 eV or lower an unphysical barrier appears. Therefore, this interface may be pinned within a more narrow range.

4. Discussion

The key to understanding the role of each layer in the front contact structure is noting the difference between the TCO/CdTe, TCO/HRT/CdTe, TCO/CdS/CdTe, and TCO/HRT/CdS/CdTe devices. Differences in carrier concentration or resistivity of the material

(which has been widely discussed), the existence of pinholes and other morphological imperfections, their crystallographic mismatch, and band alignment with CdTe all affect recombination at the junction.

The common theory states that pinholes where there is no CdS cause weak diodes which shunt current away from stronger CdS/CdTe diodes. This was not justified by experimental evidence since cells have not shown increasing pinhole density or area with thinner CdS layers. Furthermore, pinholes do not seem to have as large an effect on device efficiency as a simple parallel diode model (allowing for unlimited forward current densities) suggests [16]. This theory also fails to explain why devices without CdS are typically of poor quality and the dependence of device parameters on thickness is independent of whether pinholes exist.

4.1. Lattice Mismatch

One theory that holds true for single crystal, epitaxially-grown devices is that the lattice constant between the absorber and underlying material must match closely in order to provide a good growth template, which will minimize defects in the material. In single crystals, strain due to mismatch is relieved by the creation of threading dislocations which continue through the entire thickness of the material. To reduce interface recombination, a good crystallographic match is considered important to reduce the interface defect density, and to provide a growth template which minimizes defects in the CdTe bulk. CdS has a lattice mismatch of 10% with CdTe, and only inter-

diffuses slightly during high-temperature device processing [28]. Since $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ has the same crystal structure and a lower lattice constant than both ZnO and CdS , it possesses greater mismatch to CdTe and would not produce a high-quality device if lattice matching were a paramount consideration. In polycrystalline materials, there is already a relatively high concentration of interface defects, and strain can be relieved at grain boundaries, terminating dislocations. Therefore, rules that are predictive in single-crystal epitaxial devices may not apply equally well to these less ideal materials. Still, improving the quality of this interface may prove important to voltage increases above the current state of the art. Adding a patterned insulating oxide with nanoscale CdS contacts is one way of creating single-crystal CdTe islands, and may improve growth of the CdTe by preventing dislocations and other defects in the CdTe absorber [29, 30].

4.2. Band alignment of CdTe front contacts

The ideal front contact of the heterojunction will maximize the built-in potential by holding the Fermi level near the conduction band minimum of CdTe in equilibrium and minimize interface recombination at the front CdTe interface. To achieve this, a flat or slightly positive CBO (spike) is desirable, and a negative CBO (cliff) would lead to reduced built-in potential and greater interface recombination; here, cliff and spike are defined as in Figure 1 of Klenk [31]. The front contact structure also serves to provide a low-resistance contact for electrons; therefore, the positive conduction band offset must be small

or else a secondary barrier (kink) will appear in the current-voltage curve of the cell. The electron affinity of the HRT, including any effects of interface charge, is a key predictor of HRT performance. Negatively charged acceptor defects at the interface have a similar effect to a high electron affinity contact material, and these defects would change dependent on the specific combination of materials at the interface. These defects do not appear to dominate the interfaces in question, but could be a cause of scatter in the data.

Commonly used values for the tin oxide electron affinity indicate that this layer has a relatively flat conduction band alignment with CdTe [27]. The band alignment of the SnO_2/CdS interface has been investigated both by progressive growth of CdS [32] and by sputter depth profiling [33]. It was reported that the offset at this interface was $\Delta E_C = -0.1$ eV. This was measured after the full thickness of CdS was deposited and not immediately at the interface. The authors observed the Fermi level to be well below the conduction band in the CdS with band bending away from the interface, resulting in a total barrier height of 0.4 eV. An earlier study by Niles *et al.* reported a flat conduction band at the interface [34]. However, recent studies specifically of fluorine-doped tin oxide report a work function of 5 eV [35], much higher than commonly used for SnO_2 in CdTe device modeling; if true, then a CdTe heterojunction with FTO or a device with thin CdS would create a cliff alignment. Klein reports that there is a wide

variation of more than 1 eV in the work function of SnO_2 , which cannot be accounted for by a difference in doping [36]. Furthermore, because FTO is degenerately doped, the Fermi level is reported to be up to 0.6 eV above the conduction band minimum [35]. With Fermi level pinning at the CdTe conduction band minimum, this would in itself create a cliff band alignment at the front interface. It appears that the work function and electron affinity of tin oxide with different dopants and alloy materials is highly variable, and a single value cannot account for all processing variables.

As a wide-bandgap, n-type semiconductor, FTO can be used directly as the front contact of the solar cell. As reported here and by others [9], a FTO/CdTe junction results in a cell with very low open-circuit voltage, while a tin oxide-based HRT/CdTe junction produces an open-circuit voltage intermediate to FTO/CdTe and CdS/CdTe junctions. None of these devices necessarily has low shunt resistance.

Crossover of the light and dark curves is a common phenomenon seen in thin-film solar cells. This has been explained as a conduction band “spike” between the absorber and CdS that is slightly reduced due to photoconductivity in the CdS layer [20]. Without any CdS layer, charged defects at the TCO/CdTe interface rather than charged defects in the CdS can explain the light-dependent effect and would cause unfavorable band alignment. An effect similar to that of an HRT has been demonstrated simply by plasma treatment of the TCO, which affects at most a few

tens of nanometers of the surface [37], further indicating that interface charge is in part responsible for unfavorable band alignment.

The $\text{SnO}_2\text{:F}/\text{CdTe}$ band alignment is far from ideal, and device results here indicate that some HRT materials which increase the resistivity of this material but do not change the electron affinity appreciably, such as the nitrogen-doped $\text{SnO}_2\text{:F}$, produce no improvement in cell performance. Materials that have lower electron affinity produce the desired HRT effect. The ZnO-MgO alloys provide a model system for testing the effects of electron affinity, since ZnO is known to perform moderately well as an HRT layer, and adding magnesium changes the electron affinity of this layer without significant changes to the crystalline structure, resistivity, or deposition process. Improved device performance with the elimination of CdS was demonstrated, and both cliff and spike behavior could be demonstrated by varying thickness and composition of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ layer.

5. Conclusions

Pinholes do not seem to be the primary cause of effects seen relative to CdS layer thickness. The existence of a wurtzite $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ layer that can produce a high open-circuit voltage without CdS, but has a larger lattice mismatch with CdTe relative to CdS or ZnO, implies also that lattice matching is not the key factor for producing an effective front contact to CdTe. In contrast, band alignment considerations have consistently predicted the performance of front

contact layers, including with sputtered, oxygenated CdS layers [4].

While sparsely explored in the CdTe literature, the importance of band alignment at the front contact has been well explored and confirmed in Cu(In,Ga)Se₂ thin-film solar cells, such as with Mg_xZn_{1-x}O layers. The weakness of the TCO/CdTe diode appears to derive from unfavorable band alignment of the TCO layer with CdTe, from a combination of electron affinity, charged defects, and degenerate doping. This causes a strong, light-sensitive barrier to form in addition to the poor device properties of TCO/CdTe junctions. HRT layers, which are not degenerately doped, can have a wide range of effectiveness in improving contact properties. The SnO₂-based HRT layers shown here have a wide range of effectiveness which correlates with electron affinity. In the case of very poor band alignment between oxide and CdTe, CdS-based layers that are very thin or have low carrier concentration do not produce high-efficiency devices; however, a thin, resistive 50-nm layer of Mg_xZn_{1-x} with optimized band alignment can replace both the HRT and CdS layers. In short, band alignment concerns appear to explain interface phenomena where other variables such as fractional pinhole area and lattice mismatch do not, and account for the inconsistent behavior of HRT materials with high resistivity.

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Oxide	ϕ [eV]	$E_F - E_V$ [eV]	χ [eV]	d [nm]	ρ [Ω -cm]	alloy composition [at%]
SnO ₂ :Zn (low)	4.1	3.9	4.4	150	5	0.8
SnO ₂ :Ga	4.3	3.9	4.6	150	10	0.9
SnO ₂ :In	4.4	3.8	4.6	150	80	0.5
SnO ₂ :Zn (high)	4.7	3.7	4.8	150	100	3.3
SnO ₂ :F,N	4.9	3.9	5.2	95	100	0.2
SnO ₂	5.0	3.9	5.3	150	no data	0
SnO ₂ :F (TCO)	5.0	3.9	5.3	400	$5 \cdot 10^{-4}$	0.3
ZnO	4.3	3.3	4.4	50	$\approx 10^7$	0
Mg _x Zn _{1-x} O	4.0	3.8	4.1	50	$\approx 10^7$	23

Table 1: UPS band measurements of various oxides deposited on FTO are summarized. The valence band positions and material bandgaps were used to calculate electron affinity.

Parameter	Oxide	CdS	CdTe
x [nm]	150	none or 50	2500
E_G [eV]	3.6	2.4	1.5
χ [eV]	varies	4.5	4.4
$\varepsilon/\varepsilon_0$	9	10	9.4
N_C [cm ⁻³]	$2.2 \cdot 10^{18}$	$2.2 \cdot 10^{18}$	$8.0 \cdot 10^{17}$
N_V [cm ⁻³]	$1.8 \cdot 10^{19}$	$1.8 \cdot 10^{19}$	$1.8 \cdot 10^{19}$
μ_e [cm ² /V·s]	1	100	320
μ_h [cm ² /V·s]	25	25	40
τ_n, τ_p [ns]	0.1	0.1	2
n or p [cm ⁻³]	n = $1 \cdot 10^{18}$	n = $1 \cdot 10^{15}$	p = $2 \cdot 10^{14}$
	Oxide/CdTe	CdS/CdTe	CdTe Back
S_n, S_p [cm/s]	10^7	10^5	10^7
Q_{if} [cm ⁻²]	$-2 \cdot 10^{12}$	-	-

Table 2: 1-d modeling baseline parameters used for SCAPS simulation of HRT and window material property effects.

Figure 1: Efficiency parameters of cells made with varying sublimated CdS thickness, adapted from previous work [16]. Cells were made with TCO/CdS/CdTe and TCO/HRT/CdS/CdTe structures. The highest efficiency for a cell with the optimum Zn-doped SnO₂ HRT occurs with slightly thinner CdS than for devices without HRT.

Figure 2: J-V curves of highest-efficiency cells with the TCO/CdTe, TCO/HRT/CdTe, TCO/CdS/CdTe, and TCO/HRT/CdS/CdTe structures using the Zn-doped SnO_2 HRT. The HRT allows additional short circuit current from thinner CdS, with minimal loss in V_{OC} . Maximum efficiency was improved from 12.9% to 13.8%.

Figure 3: Series resistance of a device with the TCO/CdTe structure. a) Each curve has a different level of blue LED illumination (over several orders of magnitude). Series resistance is reduced drastically with increasing illumination. b) The dependence of series resistance on J_{SC} (a measure of illumination level) is comparable for illumination with red and blue light.

Figure 4: a) The transmission of the films remains high over a wide wavelength range. b) The Tauc plot shows increasing optical bandgap with magnesium content.

Figure 5: Parameters are shown for devices made with $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ layers on TEC 10 glass with no CdS layer. With higher magnesium, high V_{OC} can be achieved with thinner layers but fill factor is reduced due to a kink in the J-V curve. Error bars show the 95% confidence interval.

Figure 6: The J-V curves of the center devices from the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thickness-composition optimization for 100-nm thick MZO layers. The ZnO sample has low V_{OC} , while the samples with higher magnesium composition have high V_{OC} and a kink; there is variability in the kink, with a trend toward a larger kink and lower fill factor with higher magnesium content and thicker MZO layers.

Figure 7: Comparing UPS measurements of electron affinity with device results, a) when no CdS is deposited and CdTe is grown on oxides, there is a strong correlation between V_{OC} and electron affinity. b) the correlation is somewhat weaker when a resistive oxygenated CdS window layer is used between the oxide and CdTe; and c) the dependence is quite weak but present when sublimated CdS was used.

Figure 8: Using X-ray emission spectroscopy to probe the valence band and X-ray absorption spectroscopy to probe the conduction band, a clear shift to higher photon energy is seen for the HRT versus the TCO, implying lower electron affinity.

Figure 9: a) For devices with no CdS, the conduction band offset goes from positive to negative as the electron affinity of the oxide increases. This causes the CdTe conduction band minimum to move away from the Fermi level. b) The effect of electron affinity on device quality is clearly seen in the model results. With a small spike the V_{OC} can be improved from a flat conduction band offset, and with a large spike (low electron affinity) a kink appears in the J-V curve.

Figure 10: The experimental band measurements and device results are compared to the model a) For devices with no CdS and b) for devices with 50 nm CdS. The voltage is less sensitive to small changes in conduction band offset, and the oxide/CdS interface is pinned in a limited range of conduction band offset.