Graphical Abstract

Evolution of oxygenated cadmium sulfide (CdS:O) during high-temperature CdTe solar cell fabrication

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Abstract

Oxygenated cadmium sulfide (CdS:O) produced by reactive sputtering has emerged as a promising alternative to conventional CdS for use as the *n*-type window layer in CdTe solar cells. Here, complementary techniques are used to expose the window layer (CdS or CdS:O) in completed superstrate devices and combined with a suite of materials characterization to elucidate its evolution during high temperature device processing. During device fabrication amorphous CdS:O undergoes significant interdiffusion with CdTe and recrystallization, forming CdS_{1-y}Te_y nanocrystals whose Te fraction approaches solubility limits. Significant oxygen remains after processing, concentrated in sulfate clusters dispersed among the CdS_{1-y}Te_y alloy phase, accounting for ~30% of the post-processed window layer based on cross-sectional microscopy. Interdiffusion and recrystallization are observed in devices with un-oxygenated CdS, but to a much lesser extent. Etching experiments suggest that the CdS thickness is minimally changed during processing, but the CdS:O window layer is reduced from 100 nm to 60-80 nm, which is confirmed by microscopy. Alloying reduces the band gap of the CdS:O window layer to 2.15 eV, but reductions in thickness and areal density improve its transmission spectrum, which is well matched to device quantum efficiency. The changes to the window layer

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4 in the reactive environments of device fabrication are profoundly different than what occurs by
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6 thermal annealing in an inert environment, which produced films with a band gap of 2.4 eV for
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8 both CdS and CdS:O. These results illustrate for the first time the significant changes that occur
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10 to the window layer during processing that are critical to the performance of CdTe solar cells.
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16 Keywords: cadmium telluride; cadmium sulfide; oxygen; interdiffusion; liftoff; characterization

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1. Introduction

Cadmium telluride (CdTe) has emerged as the leading thin-film photovoltaic (PV) technology and is poised to reach grid parity soon with record device efficiency currently at 21.5% [1].

Cadmium sulfide (CdS) is the most commonly used window layer in CdTe photovoltaic devices [2]. This layer provides a receptive surface for CdTe nucleation and growth, and forms a high quality heterojunction with the absorber. Light absorbed by CdS does not generate photocurrent, so quantum efficiency (QE) is attenuated at wavelengths below the CdS band gap (520 nm) [3]. Photocurrent losses can be decreased by reducing thickness, but only to a degree. As the CdS thickness is reduced efficiency can decline due to deterioration in both open circuit voltage (V_{oc}) and fill factor (FF) [4, 5]. The CdS window layer can be deposited by several techniques, including chemical bath deposition (CBD) [6], close-spaced sublimation (CSS) [7], evaporation [8], and sputtering [9]. Sputtering offers numerous advantages over alternative deposition methods. Like CSS and evaporation it is vacuum-based and scalable for in-line manufacturing, and uniformity and waste management are less problematic for vapor deposition compared to solution-based methods. Most significantly, sputtering enables the ability to finely tune the window layer composition and properties by simply varying the argon/oxygen fraction [10].

The role of oxygen in CdS has been a focus of study for decades. It has been observed that CdS deposited by physical vapor deposition in the absence of oxygen undergoes extensive interdiffusion with CdTe during high temperature processing [11, 12]. Interdiffusion reduces the effective thickness of the window layer, creating $CdS_{1-y}Te_y$ alloys whose optical band gap E_g is given by

$$E_g(y) = 2.40(1 - y) + 1.51(y) - b(1 - y)(y) \quad [eV] \quad (1)$$

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4 where y refers to the atomic concentration in $\text{CdS}_{1-y}\text{Te}_y$ and b is a bowing parameter equal to
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6 ~ 1.8 [13]. Alloying reduces the band gap of the window layer, and excessive interdiffusion
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8 degrades device performance by reducing the short circuit current density (J_{sc}) and/or by
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10 shunting caused by localized disappearance of the window layer [8, 14].
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14 The presence of oxygen in CdS has been found to have a dramatic impact on the
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16 interdiffusion process. McCandless and Birkmire [15] showed that annealing CdS in a
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18 $\text{CdCl}_2:\text{O}_2:\text{Ar}$ environment prior to CdTe deposition eliminated the formation of $\text{CdS}_{1-y}\text{Te}_y$ on the
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20 S-rich side of the junction, attributing this behavior to oxide formation along grain boundaries.
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22 Oxygen is present in CBD films at levels of 5–15 at. %, and its presence is credited with
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24 retarding interdiffusion in a similar manner as O_2 annealing [14]. The higher level of oxygen in
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26 CBD CdS is thought to be responsible for producing higher efficiency than devices fabricated
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28 using CdS deposited by CSS or evaporation. Oxygenated cadmium sulfide ($\text{CdS}:\text{O}$) was first
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30 introduced in 2002 by Wu and co-workers [10], who prepared window layers by reactive
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32 sputtering using a CdS target in an O_2/Ar ambient. Based on transmission electron microscopy
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34 (TEM) images, these authors also attributed the observed improvements in J_{sc} to the ability of
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36 $\text{CdS}:\text{O}$ to suppress Te interdiffusion and alloy formation [16].
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43 CBD has remained one of the leading techniques to prepare CdS, particularly in research
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45 laboratories, though in recent years several groups have turned to sputtered $\text{CdS}:\text{O}$ to produce
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47 high efficiency devices [17-21]. With increasing amounts of oxygen in the sputter ambient, film
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49 crystallinity is reduced and the optical band gap increases. Performance gradually improves with
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51 increasing optical band gap, reaches a maximum, and then drops dramatically [17, 19, 20]. The
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53 oxygen content in as-deposited $\text{CdS}:\text{O}$ can reach 45 at. % via sulfate group (CdSO_4)
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55 incorporation [19, 20, 22]. The efficiency gains are achieved primarily through increases in J_{sc}
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4 due to improvements in short-wavelength quantum efficiency without compromising V_{oc} or FF.
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6 The successful use of CdS:O requires careful optimization of sputter conditions, but high
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8 performance devices with power conversion efficiencies ranging from 15.2–16.4% have been
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10 achieved independently by several groups [16, 17, 19, 23].
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14 The trends discussed above have been well documented, but the underlying reasons
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16 controlling the observed behavior are not fully understood. It has been suggested that the
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18 catastrophic failure observed at high oxygen levels is caused by an excessive conduction band
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20 offset between the CdTe and CdS:O layers [19], while there are several possible explanations for
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22 the improvements in J_{sc} at moderate oxygenation levels. Changes in device performance could
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24 simply reflect the enhanced transparency of as-deposited CdS:O. Alternatively, CdS:O may
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26 decompose and release oxygen during subsequent high temperature processing, resulting in a
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28 CdS layer of reduced thickness. Finally, as discussed above, the degree of interdiffusion with
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30 CdTe appears to be highly dependent on the amount of oxygen in the window layer. The
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32 evolution of the window layer during device processing has been studied fairly extensively for
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34 CBD and evaporated CdS, but has not been examined in detail for CdS:O.
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41 In the conventional superstrate architecture, the CdTe absorber is deposited directly on
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43 CdS:O at high temperature (500–600 °C) by CSS or vapor transport deposition, which is
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45 followed by an annealing step in the presence of $CdCl_2$ at $T \sim 400$ °C. These high-temperature,
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47 reactive environments likely cause significant changes to the underlying CdS:O material. For
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49 example, thermal annealing in an inert environment appears to convert CdS:O back to intrinsic
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51 CdS. Paudel et al.[21] varied the optical band gap of sputtered CdS:O films from 2.0–3.2 eV
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53 through manipulation of both oxygen content and substrate temperature. After annealing at
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55 ~600 °C in the He/O₂ ambient used during CSS all of these films exhibited properties that were
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characteristic of intrinsic CdS based on their crystal structure and band gap (~ 2.4 eV). Similar changes in optical properties were reported by Kephart et al. when annealing their films at 500 °C, but interestingly they observed that the SO_x content of these films was not significantly changed by annealing [19]. However, since CdTe vapor was not present in these experiments, it is not clear if these thermally-induced changes are truly representative of device processing.

Direct characterization of the window region with high fidelity in completed devices is extraordinarily difficult because this ~ 100 nm layer is sandwiched between a TCO-coated glass superstrate and several microns of the CdTe absorber. To better understand the evolution of CdS:O during processing and its impact on device performance we make use of two recently developed approaches to expose both sides of the window layer in completed devices [24]. It is shown that oxygenated cadmium sulfide (CdS:O) undergoes significant interdiffusion and recrystallization during CdTe device fabrication, forming $\text{CdS}_{1-y}\text{Te}_y$ nanocrystals with a band gap of 2.15 eV. Substantial oxygen is retained throughout processing, concentrating in sulfate clusters dispersed throughout the window layer. These results illustrate for the first time the significant changes that occur to the CdS:O window layer during processing that are critical to the performance of CdTe solar cells.

2. Materials and Methods

2.1 Device Fabrication

Devices in this work were fabricated in the superstrate configuration using Corning 7059 glass coated with a fluorinated and intrinsic tin oxide bilayer using chemical vapor deposition. The properties of un-oxygenated CdS were compared with moderately oxygenated CdS:O whose as-deposited optical band gaps were 2.4 and 2.8 eV, respectively. In previous studies, it was

found that the 2.8 eV CdS:O produced optimal device performance using our process [20]. Films were deposited by rf magnetron sputtering using a stoichiometric CdS target (Materion, 99.99% purity) in a Unifilm PVD-300 sputtering system. The sputtering ambient was pure argon for the intrinsic CdS films, and a 4% O₂/Ar mixture was used to produce the 2.8 eV CdS:O. Prior to deposition the system was evacuated to $\sim 2 \times 10^{-7}$ Torr and backfilled with the desired ambient. Gas flow rates were maintained at a total of 100 sccm, and a throttle valve was used to set the pressure to 15 mTorr. The sputter power density was 1.1 and 2.2 W/cm² for CdS and CdS:O films, respectively, and the film thickness was fixed at 100 nm for device fabrication. A subset as-deposited CdS/CdS:O films were subjected to thermal annealing performed at 600°C for 5 min in an inert ambient. In device fabrication, ~ 4 microns of CdTe was deposited on CdS/CdS:O layers using CSS. The source and substrate temperatures were held at 660 and 600°C, respectively, for 150 s in an oxygen/helium ambient at 16 Torr. Vapor-phase CdCl₂ annealing was also performed in a CSS configuration with source and substrate temperatures fixed at 400°C for 10 min in an oxygen/helium ambient at 400 Torr. To complete fabrication an evaporated Cu/Au back contact was used followed by annealing at 260°C for 30 min to promote Cu diffusion [25]. All devices with CdS:O had very similar performance, yielding photovoltaic conversion efficiency of $\sim 14\%$ as described previously [20, 24]. The device analyzed by transmission electron microscopy in this work was processed identically to those described above with the exception of the back contact. Instead of using Cu/Au this device was contacted with ZnTe:Cu/Au [26], and had an efficiency of 16%.

2.2 Window Isolation Techniques

Two complementary techniques were used to isolate the window layers in completed devices: selective etching and thermo-mechanical lift-off. Similar techniques have previously been applied to investigate the evolution of conventional CdS during device processing [27, 28]. Figure 1 displays schematics and photographs of the samples generated by etching (left) and lift-off (right). Selective etching of CdTe over CdS is challenging due to the chemical similarity of the two compounds. In this work a mixture of ethylenediamine ($C_2H_4(NH_2)_2$) and hydrogen peroxide was used to selectively remove CdTe [24]. Ethylenediamine is added to water to form a 50% (vol.) mixture and allowed to equilibrate in a temperature-controlled beaker before adding the sample and the limiting reagent hydrogen peroxide at 10% (vol.). The selectivity achieved using this approach is quantified below.

Figure 1. Schematics and photographs of samples prepared from completed devices by chemical etching (left) and thermo-mechanical lift-off (right).

Conventional mechanical lift-off involves using epoxy to fixture the back of the device to another substrate, and then using brute force to pull the device apart [14]. Although this approach can be successful, the yield is typically poor, and it is difficult to control with cleavage occurring

at both the TO|CdS and CdS|CdTe interfaces. The innovation introduced here exploits differences in the coefficient of thermal expansion (CTE). CdS and CdTe have nominally identical CTE values ($47, 49 \times 10^{-7}/\text{K}$), which are significantly greater than the CTE of tin oxide ($38 \times 10^{-7}/\text{K}$). The back side of the device was first bonded to an aluminum electron microscope mount (Ted Pella) using epoxy (Loctite 1c), and after curing the assembly is placed in liquid nitrogen. Upon immersion, the devices cleanly separate at the TO|CdS interface without application of external force. The lift-off approach provides a specular, mirror quality surface of the front of the window layer as well as access to the remaining TCO-coated superstrate (Figure 1) [24]. These two techniques enable facile characterization of the composition, structure, and optical properties of the window layer after processing as described below.

2.3 Characterization

The composition, structure and optoelectronic properties of the window layers isolated by these two techniques were quantified. Optical transmittance and reflectance were measured by an N&K spectrophotometer. Optical band gaps were determined using direct band gap Tauc plot analysis [29]. X-ray diffraction measurements were taken using $\theta/2\theta$ and 1° glancing incidence scans from 20 to $70^\circ 2\theta$ using Cu K α radiation on a Rigaku Ultima diffractometer. Dynamic SIMS was performed using an ION-TOF Model IV. Sputtering was carried out using 1 keV O_2 and Cs ions for the positive and negative ion spectra, respectively. In both cases a sputter beam current of 50 pA was used to sputter a $300 \times 300 \text{ }\mu\text{m}$ area. Analysis of a $100 \times 100 \text{ }\mu\text{m}$ area at the center of the sputter crater was performed using 25 keV Bi_3^+ primary ions at a current of 0.4 pA . Due to the absence of calibrated standards the intensity of each element is reported in terms of raw signal counts, and the sputter depth was estimated by comparisons with SEM images. High resolution transmission electron microscopy (HR-TEM) was the tool used to investigate the

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4 detailed microstructure of a completed device employing 2.8 eV CdS:O cells using the facilities
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6 at Loughborough. TEM samples were prepared by focused ion beam (FIB) milling using a dual
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8 beam FEI Nova 600 nanolab. A standard *in situ* lift out method described previously [30] was
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10 employed for sample preparation. HR-TEM imaging was carried out in a FEI Technai F20
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12 equipped with an Oxford Instruments X-Max 80 silicon drift detector (SDD) energy dispersive
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14 X-ray detector (EDX). EDX was used to produce chemical distribution maps of the cells as well
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16 as line scans. Due to the absence of calibration standards quantification relied on standard
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18 sensitivity factors. This was found to over-predict the density of lighter elements (O, S) that emit
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20 X-rays at low energy and as such we use EDX for relative quantification. SEM images were
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22 obtained using a FEI Helios Nanolab 600i DualBeam SEM/FIB. Acquisition and quantitative
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24 analysis of X-ray photoelectron spectroscopy (XPS) was performed by Charles Evans and
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26 Associates on samples without sputter cleaning.
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36 **3. Results**

37 *3.1 Etch Selectivity, Window Layer Consumption, and Optical Transformation*

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39 The ideal selectivity ($S_{\text{CdTe/CdS}}$) of the chemical etch was defined as the ratio of the etch rate of
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41 CdTe relative to etch rate of the as-deposited CdS(O). The ethylenediamine etch completely
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43 removes 4 μm CdTe films in ~ 90 s for beaker jacket temperatures between 10 and 50°C,
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45 conservatively placing the CdTe etch rate (ER) at >2000 nm/min. Using this value and the ER of
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47 *as-deposited* CdS and CdS:O films the minimum selectivity was determined as a function of
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49 beaker temperature as shown in Figure 2. Susceptibility to the etch varied greatly depending on
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51 the oxygenation level of the window layer and to a lesser extent jacket temperature. $S_{\text{CdTe/CdS}}$
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53 >300 was achieved for CdS sputtered in pure Ar across the 10–50 °C range explored. The
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selectivity for the optimal 2.8 eV CdS:O ranged from 50–250 with best results achieved at low temperature, whereas highly oxygenated 3.2 eV CdS:O was limited to <50. Thus, the use of this chemical etch for effectively exposing CdS:O is limited to material with a bandgap < ~3 eV, where the selectivity for CdTe over CdS:O was sufficient to ensuring minimal etching of the underlying window layer. The 3.2 eV CdS:O is not relevant to devices, but is included here to demonstrate the loss of selectivity that occurs at higher oxygen levels as it is pertinent to the discussion below.

Figure 2. Etch selectivity for CdTe over as-deposited CdS films as a function of cooling jacket temperature and degree of oxygenation.

One potential consequence of device processing is that the effective CdS thickness may be reduced through processes such as the loss of oxygen and/or sulfur/tellurium interdiffusion. To assess this possibility the thickness of the window layer after processing and etching was determined for both CdS and CdS:O samples at various stages of processing. In the following

two sections the properties of the window layer are compared in three states: 1) as-deposited; 2) after thermal annealing; and 3) after device processing and etching. Thermal annealing was performed at 600 °C in an inert environment. Device processing involved subjecting the samples to standard CdTe deposition and CdCl₂ activation followed by removal of CdTe using the selective etch. Film thicknesses were measured using profilometry, and nominally 200 nm thick window layers on glass were employed to improve the accuracy of these measurements. It was found that thermal annealing had a negligible impact on the thickness of either CdS or moderately oxygenated CdS:O (Figure S1, Supporting Information). However, after device processing and etching steps, the thickness of the un-oxygenated CdS was reduced by 13 nm. In contrast, the thickness of the moderately oxygenated cadmium sulfide was reduced by 50 nm. Device processing, presumably through interactions with CdTe, alters the composition of the window layer adjacent to CdTe to make it more susceptible to etching. The extent of these changes is much more pronounced in the case of CdS:O.

The chemical etch allows the optical properties of the window layer to be examined after device processing. The optical band gaps of CdS and CdS:O window layers in the as-deposited state, after thermal annealing, and after full device processing are compared in Figure 3. These samples employed as-deposited window layers with the standard 100 nm thickness on tin oxide-coated glass. Corresponding Tauc plots used to derive these values are shown in Figure S2, Supporting Information. As-deposited CdS had a slightly narrow band gap, perhaps caused by preferential sulfur sputtering from the substrate [31]. After annealing, the band gap of CdS recovered to the stoichiometric value of 2.4 eV. Thermal annealing of the moderately oxygenated CdS:O reduced its band gap from 2.8 to 2.4 eV. These findings are consistent with previous annealing studies of CdS/CdS:O [19, 21]. In contrast, the properties of the window

layer in completed devices are significantly different, with the optical band gap of both CdS and CdS:O window layers red shifting to ~2.2 eV. The oxygenated material was red-shifted further than the intrinsic CdS. The obvious difference between the two experiments is exposure to Te during device processing, which presumably could lead to the formation of CdS_{1-y}Te_y alloys. Using Eq. 1 the value of y for the un-oxygenated and oxygenated cadmium sulfide after processing based on their band gaps would be 0.06 and 0.10, respectively. The latter value compares favorably with the reported solubility limit of y = 0.0925 at 600 °C [12].

Figure 3. Optical band gap of window layers deposited on glass, after annealing in an inert ambient, and after device processing and etching for both intrinsic and moderately oxygenated CdS.

3.2 Structural Transformation

Figure 4 compares 1° glancing incidence X-ray diffraction (GIXRD) patterns obtained from CdS and 2.8 eV CdS:O films in the as-deposited state, after annealing, and from completed device

stacks after etching. GIXRD was used to improve surface sensitivity and minimize contributions from the underlying tin oxide layer. Sputtered CdS without oxygen is polycrystalline and highly oriented in the hexagonal (002) direction. Upon thermal annealing one additional reflection associated with the hexagonal phase is observed. Device fabrication leads to further re-crystallization with the detection of four additional reflections, though the film remains preferentially textured in the (002) orientation. In contrast, the 2.8 eV CdS:O is XRD amorphous as-deposited, but recrystallizes into the hexagonal phase upon thermal annealing, displaying a random orientation. The fully processed device undergoes similar re-crystallization, though the peak intensity is somewhat attenuated, possibly reflecting a thickness reduction as discussed in the previous section. Consistent with this supposition, the intensity of peaks due to the underlying tin oxide is considerably stronger in devices fabricated using CdS:O compared to CdS. Neither sample exhibited diffraction peaks associated with CdTe after device processing, showing that the chemical etch completely removed the overlying CdTe layer. An interesting feature in the CdS:O samples is the strong peak at $2\theta \sim 30^\circ$ that appears after annealing, but disappears upon etching. It is speculated that this may reflect the formation of CdSO₄, and that this phase is then removed by the etch. This assignment is tenuous as XRD standards are only available for various CdSO₄ hydrate phases [32]. Additional evidence in support of this hypothesis is presented below in Sections 3.4 and 3.5. GIXRD analysis of the window layer in lift-off samples confirmed these changes. The quality of the cleave at the TO|CdS interface was supported by absence of the tin oxide peaks in the lift-off sample (Figure S3, Supporting Information), and the absence of CdS peaks in the remaining glass/TCO superstrate (Figure S4, Supporting Information). Note that the $2\theta \sim 30^\circ$ peak tentatively assigned to the CdSO₄ is also observed in the GIXRD pattern of the CdS:O liftoff sample, but not the CdS sample.

Figure 4. 1° glancing incidence XRD patterns of window layers deposited on glass, after annealing in an inert ambient, and after complete device fabrication and etching for both CdS and moderately oxygenated CdS:O. Reference XRD patterns (at bottom) were used to identify hexagonal CdS and tetragonal SnO₂ [33-36].

3.3 Secondary Ion Mass Spectrometry (SIMS)

A powerful tool for characterizing CdTe devices is secondary ion mass spectrometry (SIMS) [37]. Typically CdTe devices are profiled from the back contact [38, 39], meaning several microns of CdTe must be removed prior to reaching the heterojunction and CdS. SIMS profiling creates a mixed layer whose impact grows with sputter depth, undermining the spatial resolution and accuracy of the technique. Although the front contact layers can be picked out from elemental gradients, the CdS layer is smeared out over a depth several times larger than its true thickness as a result of the ever-expanding sputter volume [14, 37]. SIMS profiling from the front contact has been performed after removing the glass superstrate [40, 41], but this requires time-intensive mechanical polishing and the use of concentrated HF acid. The techniques

developed here enable the window layer in superstrate devices to be assessed without these complications.

Figure 5 displays SIMS profiles for selected elements obtained from both lift-off (left) and etched (right) samples obtained from the same device fabricated with the optimal 2.8 eV CdS:O. Figure 5a displays the SIMS profiles obtained from the two samples for sulfur and tellurium. The beginning of the SIMS profile for the lift-off sample was placed at the CdS|TO interface ($x = 0$) and moves left into the CdTe layer. The profile for the etched sample was shifted horizontally so that the sulfur profiles overlapped in the window layer region. This placed the start of this profile at $x \sim -38$ nm, and it proceeds to the right into the tin oxide. The identical shift applied to the S profile was then applied to all remaining elemental profiles. The vertical dashed lines indicate the approximate positions of the remaining interfaces, based on gradients in elemental composition and SEM imaging. Note that the sharp aberrations at the beginning of each SIMS profile are artifacts attributed to surface contamination, and not representative of the physical profile.

Comparison of the two sulfur profiles suggests that the window layer that remains after etching is only about half as thick as the lift-off sample, and this is attributed to etching as described above. Therefore, the lift-off samples are most useful for analysis of the full window layer in completed devices. In both the etch and lift-off sample the sulfur density is approximately constant in the layer adjacent to tin oxide. Moving towards the CdTe the S intensity begins to decline around the position where the etch sample begins. The decline is initially gradual, becomes steeper at the interface between the two materials, and then decreases within the CdTe layer. Note that the sulfur content in CdTe is significant, on the order of one

Figure 5. a) SIMS profiles of S and Te obtained from devices prepared using thermo-mechanical lift-off (left) and chemical etch (right); b) SIMS profiles of O, Cl, and Cu profiles obtained from the same samples. Lift-off profiles start at the CdS|TO interface ($x = 0$) and move left into the CdTe layers, whereas the etched profiles begin at $x = -38$ nm and move right into the tin oxide.

atomic percent. Data from the etched sample shows that sulfur declines sharply as one moves into the tin oxide, and the signal quickly declines below the limits of detection.

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4 The tellurium profiles shown in Figure 5a confirm that significant interdiffusion occurred,
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6 and that there is a significant and stable amount of Te adjacent to the interface with CdS. By
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8 comparing the Te intensity in the window layer with the bulk CdTe region the level in the
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10 window layer is consistent with the 5–10 atomic % levels extracted from the optical band gap
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12 assuming alloy formation. There is good quantitative overlap between the Te profiles obtained
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14 from the lift-off and etched sample. The signal from the etched sample ends precisely where the
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16 Te content begins to increase sharply in the lift-off sample. The chemical etch rapidly removes
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18 CdTe, so it is reasonable that this Te-rich interdiffused region would also be removed during
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26 Figure 5b compares the SIMS profiles of the major impurities (O, Cl, Cu) detected in the two
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28 samples. The level of oxygen detected in the lift-off sample is quite high and nearly constant
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30 throughout the window layer. The intensity of the O signal in the window layer is only ~2.5
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32 times less than the signal originating from the tin oxide layer (~67 at. %), indicating that
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34 significant levels of oxygen remain in the window region after processing. The O signal declines
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36 precipitously near the interface with CdTe, suggesting minimal diffusion into that layer. In
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38 contrast to sulfur and tellurium, there is a significant mismatch between the O profiles obtained
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40 from the window layer of both samples. One plausible explanation for the mismatch is that the
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42 chemical etch preferentially removes oxygen-rich areas of the window layer. As discussed
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44 above, the etch removes CdS:O material with band gaps >3 eV.
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51 Chlorine is a critical impurity in CdTe devices, and Figure 5b compares the chlorine profiles
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53 obtained from the two samples. Consistent with previous literature, preferential segregation of
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55 Cl in the window layer is observed [30, 40, 42]. The Cl profile from the lift-off sample does not
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57 align well with the etch sample. In fact, the Cl profile in the etched sample has the inverse shape
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of the O profile, suggesting that the distribution of these two elements may be interrelated. Copper is introduced at the back of the device prior to or during metallization [25], and plays a critical role in CdTe devices [43, 44]. Cu is a fast grain boundary diffuser that will migrate during the annealing steps used to activate the back contact [45]. The accumulation of Cu in CdS is thought to be detrimental to performance, and has been suggested as a contributor to device degradation [46]. SIMS is often used to understand the Cu distribution, but conventional profiling is performed from the back of the device [26, 38], which limits its sensitivity in the heterojunction region. As shown in Figure 5b there is good overlap in the Cu profiles obtained from the two samples. Though the absolute intensity is low, it clearly shows that detectable levels of Cu segregate to this layer while the intensity is negligible in the adjacent CdTe and SnO₂ layers. It is notoriously difficult to quantify Cu in CdTe due to the overlap between Cu⁺ and doubly ionized Te²⁺ [47]. However if Te²⁺ ions were significantly contributing to the copper signal, one would expect the signal to be stronger in the CdTe region, but in this region the signal is below the detection limit. Moreover, the Cu signal is nominally identical in the etch sample in which the CdTe has been removed.

3.4 High-Resolution Transmission Electron Microscopy (HR-TEM)

The results presented above suggest that the amorphous CdS:O undergoes profound changes in composition, structure, and thickness during device processing. To provide further validation of these observations, high-resolution transmission electron microscopy (HR-TEM) imaging and energy dispersive X-ray (EDX) spectroscopy were employed on a completed device. Figure 6a

Figure 6. (a) HR-TEM image and associated elemental maps obtained from the heterojunction region of a completed device employing moderately oxygenated CdS:O. EDX line scans across window layer at positions (b) where O is not present and (c) crossing an O-rich cluster as indicated in O atom contour map.

displays a high angular annular dark field (HAADF) micrograph and elemental concentration maps for chlorine, tellurium, oxygen, sulfur, and cadmium from a device cross section focused

on the heterojunction region. The HAADF image shows that the window layer is well-defined, forming rather abrupt interfaces with both tin oxide and CdTe. Comparison with the 100 nm vertical scale bars clearly shows that the thickness of the window layer has been reduced during device fabrication. The remaining thickness varies from 50–80 nm across the sample. The 50 nm that was removed during etching of the CdS:O test structure would serve as an upper limit for consumption, as it assumes perfect selectivity and employed window layers that were initially 200 nm thick. The TEM observations are very consistent with the estimates of consumption provided by the etch measurements. Moreover, the presence of well-defined grains is consistent with the recrystallization observed by XRD.

In the EDX mapping the color intensity scales with concentration, providing a qualitative description of the elemental distribution in this material. Chlorine is dispersed throughout the cross section, most prominently at grain boundaries in the window layer and CdTe. Decoration of these locations has been well-documented in the literature [47, 48]. Recent XPS profiling has shown that Cl preferentially accumulates in CdS at levels of ~1 at. % after CdCl₂ treatment [42], and both the EDX mapping and SIMS profile are consistent with this expectation. The tellurium map is near-uniform in the CdTe layer, and the Te concentration there is high enough in relation to the window layer that it is unclear whether a significant amount has diffused into the CdS. The base of the O map shows a uniform intensity reflecting the ~67 at. % present in the tin oxide. It is clear that the window layer contains significant levels of oxygen after processing, but it is randomly distributed in clusters throughout the window layer. Recall that in the SIMS profile of the lift-off sample a uniform oxygen profile is observed, which is expected as the lateral variations displayed here in TEM would be averaged out in the 1D SIMS profiles. Oxygen is not detected by EDX in the CdTe absorber, consistent with SIMS profiling. The S and Cd maps are

also very interesting. Much like O, the distribution of these elements is highly non-uniform within the window layer region. In fact, close comparison among these three elements shows that regions of elevated O density are well correlated to regions where both the S and Cd signals are attenuated.

For quantitative analysis, EDX line scans were performed across the window layer at positions with and without significant O present at the positions indicated in the O contour map (Figure 6a). Across the region without oxygen present (Figure 6b) there is a ~25 nm region characterized by strong S-Te interdiffusion as one moves out of CdTe, followed by ~80 nm of a $\text{CdS}_{1-y}\text{Te}_y$ phase where the alloy composition is essentially constant throughout until abruptly ending at the TO interface. Note that O was only detected in the tin oxide layer in this scan. The scan across the O-rich region (Figure 6c) is initially quite similar, with a ~25 nm of Te-S interdiffusion followed by ~40 nm of a homogeneous alloy phase. However at this point a large fraction of O abruptly appears, Te falls below detection limits, and for the next 40 nm until the TO interface the composition is characteristic of cadmium sulfate (CdSO_4).

3.5 SEM and X-ray Photoelectron Spectroscopy (XPS)

Figure 6 suggests that oxygen segregates during processing, forming sulfate-rich domains and leaving oxygen-free $\text{CdS}_{1-y}\text{Te}_y$ nanocrystals. The chemical etch would be expected to remove sulfate phase, leaving $\text{CdS}_{1-y}\text{Te}_y$ nanocrystals. The appearance and disappearance of the XRD peak at $2\theta = 30^\circ$, tentatively assigned to CdSO_4 , is consistent with this picture. Compelling confirmation of this explanation is provided by SEM imaging and X-ray photoelectron spectroscopy (XPS). Figure 7 shows a cross-sectional SEM image from the etched sample used for SIMS analysis after FIB preparation. The layers present in this image include the glass

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4 superstrate, the CVD-deposited tin oxide bilayer, the remaining window layer, and the Pt cap
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6 introduced during sample preparation. In contrast to Figure 6, the window layer is no longer
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8 contiguous, but contains individual nanocrystals separated by voids. The thickness of these
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10 nanocrystals ranges from 30–100 nm, and this is exactly the morphology one might expect if the
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12 O-rich domains shown in Figure 6 were removed. Figure 7 helps explain the odd behavior
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14 observed in SIMS profiles obtained from the etched sample. Presuming that the etch removes
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16 oxygen from that sample, the O signal in Figure 5b is then due to tin oxide, which is not
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18 unreasonable since tin oxide is exposed in ~1/3 of the cross section. Likewise, if Cl in the
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20 window layer is concentrated in or around the $\text{CdS}_{1-y}\text{Te}_y$ nanocrystals and remains through the
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22 etch, it would explain the high intensity initially observed. Finally the effective thickness of the
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24 window layer in the SIMS profile was 38 nm, reflecting a combination of the reduction in
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26 thickness and its discontinuous nature.
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Figure 7. Cross-sectional SEM image of a completed device employing moderately oxygenated CdS:O after removal of CdTe by chemical etching. The voids between nanocrystals are attributed to sulfate rich domains that were removed during etching. The Pt cap was introduced during FIB preparation of the sample.

Figure 8 compares high-resolution XPS spectra of the S 2p region obtained from the lift-off and etched samples. The lift off sample contains a mixture of sulfate and sulfide peaks, with the former dominating and accounting for 77% of the sulfur present. In contrast, the sulfur present in the etch sample is almost exclusively in the form of sulfide (95%), with the residual sulfate signal being attributed to surface contamination as observed previously with intrinsic CdS [20]. The discontinuous nature of the window layer after etching shown in Figure 7 was confirmed, as a significant level of Sn was detected by XPS. Due to its high surface sensitivity Sn would not be detected by XPS if it was covered by a continuous film. Note that tin was not detected in the

lift-off sample, providing further verification of the clean nature of the cleaved interface provided by this technique.

Figure 8. High-resolution XPS spectra from the S 2p region obtained from the lift-off sample (red) and the etched sample (blue).

XPS provided quantitative confirmation of the degree of Te interdiffusion and alloy formation observed in SIMS and estimated by optical transmission. Assuming the etched surface is composed of $\text{CdS}_{1-y}\text{Te}_y$ nanocrystals, XPS places the alloy composition at $y = \text{Te}/(\text{S} + \text{Te}) = 0.076$, which is similar to the value inferred from the optical band gap ($y = 0.10$). As described above, the chemical etch rapidly removes CdTe, so the etch may leave the surface of the nanocrystals somewhat Te-poor, explaining the small discrepancy between these two values. Significant Te was also observed by XPS in the lift-off sample adjacent to the TO, confirming its diffusion through the window layer.

4. Discussion

The two isolation techniques are complementary, exposing opposite sides of the window layer.

The primary benefit of the chemical etch is that it provides optical access to the window layer after processing. One drawback is its imperfect selectivity, especially in CdS containing significant levels of oxygen and/or tellurium, but this facet proved to be useful as a means to assess the degree of Te interdiffusion and oxygen segregation. The advantage of the lift-off technique is that it partitions the device cleanly at the TO/CdS interface, leaving the window layer and heterojunction region intact for analysis.

Coupled to the information provided by the characterization suite, it is shown that the changes caused by the reactive environments used in device processing are profoundly different than what occurs during thermal annealing. The CdS:O layer, initially 100 nm thick and amorphous, is transformed into a ~70 nm thick film consisting of $\text{CdS}_{1-y}\text{Te}_y$ nanocrystals and sulfate-rich domains. The optical band gap of the alloy suggests that the Te fraction approaches solubility limits as confirmed by XPS. SIMS and EDX profiling shows that between CdTe and the alloy phase there is a ~25 nm region characterized by strong S-Te interdiffusion, and it is postulated that this interdiffused region is removed by the chemical etch. Significant levels of oxygen are retained through device processing, segregating into sulfate clusters dispersed throughout the window layer. Alloy formation is also observed in devices employing CdS, but the level of interdiffusion and the extent of window layer consumption during processing is significantly less.

These observations contradict the prevailing opinion that the presence of oxygen within the CdS significantly inhibits interdiffusion and $\text{CdS}_{1-y}\text{Te}_y$ alloy formation [14, 15]. However, there are a few significant differences between the materials and processes used here and those

employed in most previous studies. Perhaps most important is crystallinity. CdS films deposited by either physical vapor deposition or CBD are polycrystalline. Transport occurs predominantly through grain boundary diffusion in polycrystalline CdTe devices [2, 11, 47], and oxidation of grain boundaries is a plausible mechanism to inhibit diffusion [15]. In contrast, sputtered CdS:O is amorphous as-deposited, so it is reasonable to suggest that diffusion occurs by a different, more efficient mechanism. The second major difference is the nature and absolute quantity of oxygen present in CdS:O. CBD CdS may contain as much as 15 at. % O [14, 15], but sputtered CdS:O contains more than twice that amount. In sputtered CdS:O oxygen is present almost exclusively in the form of sulfate groups [19, 20, 22], while in CBD CdS O exists in substantially different forms including hydroxide [49], carbonate groups [50], and/or water [50, 51]. Oxygen may directly promote efficient exchange among the group VI elements. Based on SIMS and XPS measurements Kranz et al. proposed that sulfur diffuses through CdTe by exchanging with oxygen [47]. Likewise, McCandless and Sites [2] indicated that the addition of O₂ during CdCl₂ annealing increases both bulk and grain boundary diffusion. In these latter two studies the oxygen levels were very low (<1 at. %), as oxygen was introduced during annealing treatments. In CdS:O where both S and O concentrations exceed 10 at. %, such processes may be very efficient. The third significant difference is the high temperature used during CdTe deposition (600 °C). Many previous studies of interdiffusion have employed CdTe deposited at lower temperature and/or used substrate configurations where CdS is deposited onto CdTe. The processing temperatures in these studies did not exceed the ~400 °C level used during CdCl₂ treatment. The composition of CdS_{1-y}Te_y in completed devices approached solubility limits, suggesting the importance of thermodynamics. At 400 °C the maximum degree of tellurium

alloying is just $y \sim 0.025$ [52], so the dramatic transformations described here would not be expected in devices processed at lower temperature.

The outstanding question that remains is how the physical changes described here contribute to the improved J_{sc} observed in device performance. Two possibilities are considered. First, the improvement in blue QE may stem primarily from thickness reductions that overcome the bandgap narrowing associated with alloy formation. The sulfate-rich domains are expected to be transparent to visible radiation [19], and the microscopy images shown in Figures 6 and 7 suggest that this phase may account for $\sim 30\%$ of the window layer, further enhancing its transparency. The second possibility is that unlike CdS, the $CdS_{1-y}Te_y$ alloy may have some degree of photoactivity that contributes to current generation. To test these possibilities, we compare device external quantum efficiency (EQE) with the transmission of the window layer isolated by chemical etching from that same sample (Figure 9). There is generally good agreement from 300 nm until onset of the CdTe band edge at ~ 850 nm, supporting the thickness reduction argument.

Figure 9. Comparison of the EQE from a completed device as well as the transmittance of the window layer from that same device after chemical etching.

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5 Finally, it is well known that impurities such as O, Cl, and Cu accumulate in the window
6 layer region and can have a profound influence on device performance. It is quite difficult to
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8 examine this region in completed devices without the benefit of techniques such as TEM or atom
9 probe tomography that require complicated sample preparation. The lift-off technique cleanly
10 separates the device at the TO/CdS interface, leaving the window layer intact for characterization
11 by profiling techniques such as SIMS, XPS, or Auger spectroscopies that can assess not just the
12 presence of impurities, but their bonding nature within the window layer. The lift-off technique
13 provides a powerful tool that could be used routinely to interrogate the nature of the
14 heterojunction region as a function of processing conditions or to better understand its evolution
15 during accelerated lifetime testing.
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32 **5. Conclusions**

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34 Two novel approaches for isolating the CdS window layer in completed CdTe solar cells are
35 presented that are distinguished by their ease of execution, reproducibility, and quality of
36 isolation. Characterization of the resulting samples demonstrate that CdS:O is dramatically
37 altered by the reactive environments of device processing in ways that are significantly different
38 than thermal annealing. CdS:O is transformed into a $\text{CdS}_{1-y}\text{Te}_y$ alloy whose composition
39 approaches solubility limits, suggesting the high temperature used during CdTe deposition drive
40 the observed changes. A substantial fraction of oxygen remains through device processing,
41 segregated into sulfate rich clusters distributed throughout the post-processed window layer. In
42 contrast to expectation, the degree of Te interdiffusion and recrystallization is significantly
43 greater when using CdS:O relative to CdS, and it is suggested that differences in initial crystal
44 structure may be the reason. It is shown that the reduced thickness and areal coverage of the
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CdS_{1-y}Te_y layer is the primary factor for the experimentally observed improvements in blue QE and efficiency. Understanding the semiconductor properties of CdS_{1-y}Te_y alloys will be critical to both understanding current device technology and improving upon it.

Acknowledgements

DMM, MOR, JMB, HPM, WKM, and TMB gratefully acknowledge funding from the U.S. Department of Energy through the SunShot Foundational Program to Advance Cell Efficiency (F-PACE) under Contract No. DE-AC36-08-GO28308. CWW, MCL and CAW were funded by the Bay Area Photovoltaic Consortium (BAPVC, Award No. DE-EE0004946). AA and JMW were funded by UKERC through the EPSRC Supergen SuperSolar Hub. We thank F. Fumasi and Dr. S. Golledge for assistance with SIMS, and K. Langworthy for assistance with SEM.

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