DEVELOPMENT OF TERNARY OXIDES FOR USE IN ADVANCED FRONT CONTACTS
IN CADMIUM TELLURIDE SOLAR CELLS BY MAGNETRON SPUTTERING

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemical Engineering).

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ABSTRACT

Cadmium telluride (CdTe) solar cells are a commercially proven photovoltaic technology. Devices are composed of thin films which enable conversion of incident sunlight into electrical carriers and simultaneous transport of these carriers to an external load. At the front of the device, the layers should be highly transparent to minimize parasitic absorption while also supporting electron transport to the external load. In this thesis, two sputter-deposited front contact layers were investigated with the goal of improving both processing and materials science understanding.

The first material investigated in this work was cadmium stannate (Cd$_2$SnO$_4$; CTO), a high-performance transparent conductive oxide (TCO). CTO, though used less frequently than on-line deposited fluorine-doped tin oxide, exhibits high transmission (>90%) and low resistivity (<4×10^{-4} Ω-cm) that are generally superior. Here, an attempt is made to demonstrate that CTO has a wide processing window, develop additional processing routes, and provide materials science insights for fabricating high-quality material. In the conventional processing scheme, as-deposited films are annealed in contact with a secondary CdS film. Films processed using this “proximity anneal” exhibited resistivities of ~2.2×10^{-4} Ω-cm and transmittance >90% when oxygen was present in the sputtering ambient in the range 600–700 °C. Sputtered CTO and bilayer CTO/CdS films were annealed in contact with bare glass and in an uncovered configuration. The thin CdS layer in bilayer films was adequate to maintain or reduce resistivity when using the covered anneal, while it enabled improved mobility and transmittance for the uncovered anneal. Stoichiometry adjustment to a higher cadmium/tin ratio was found to be
primarily responsible for increased carrier concentration, both through the proximity anneal and the covered anneal.

Next, the CdS window layer was investigated. Important structural, optical, and electronic properties were altered by varying the sputtering ambient composition (oxygen/argon). Incorporation of oxygen in the films causes the films to lose crystallinity and increases the optical band gap through a shift in conduction band energy. CdS and oxygenated CdS (CdS:O) layers were incorporated in complete devices. Maximum efficiency >14% was achieved using a CdS:O layer containing ~40 atomic % oxygen and an optical band gap of 2.8 eV. Processing was scaled up to two higher throughput systems, in which different ambient compositions were required to achieve the optimal band gap. Similar device efficiencies of 13–15% were achieved by maintaining the window layer thickness at 100 nm and the optical band gap at 2.8 eV for each system/target combination.

It is notoriously difficult to characterize the window layer and electrical junction in completed devices, because (1) they are buried between the glass on one side and a “thick” ~5-μm CdTe layer on the back, and (2) the CdS and CdTe layers are chemically similar. Two techniques were developed to enable characterization of the CdS window layer and CdS/CdTe junction in completed devices. First, a chemical etch was used to selectively etch the CdTe layer. Second, a thermo-mechanical lift-off was used to cleave the device stack at the SnO$_2$/CdS interface. Analysis of the resulting structures indicates that the high-temperature CdTe deposition and annealing steps radically alter the CdS window layer properties, including a shift in the optical band gap to ~2.2 eV, recrystallization to the hexagonal phase, and consumption of the window layer. These observations are used to explain the window layer transformations during processing and explain quantum efficiency trends observed in the previous section.
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<tr>
<td>CdCl₂</td>
<td>cadmium chloride</td>
</tr>
<tr>
<td>CdO</td>
<td>cadmium oxide</td>
</tr>
<tr>
<td>CdS</td>
<td>cadmium sulfide</td>
</tr>
<tr>
<td>CdS:O</td>
<td>oxygenated cadmium sulfide</td>
</tr>
<tr>
<td>CdTe</td>
<td>cadmium telluride</td>
</tr>
<tr>
<td>CTO</td>
<td>cadmium stannate</td>
</tr>
<tr>
<td>E&lt;sub&gt;g&lt;/sub&gt;</td>
<td>optical band gap</td>
</tr>
<tr>
<td>ER</td>
<td>etch rate</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine-doped tin oxide</td>
</tr>
<tr>
<td>HRT</td>
<td>highly resistive and transparent</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>J&lt;sub&gt;sc&lt;/sub&gt;</td>
<td>short-circuit current density</td>
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<td>metal-organic chemical vapor deposition</td>
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<td>near-infrared</td>
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<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
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<td>P&lt;sub&gt;illumination&lt;/sub&gt;</td>
<td>illuminating power</td>
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<td>RBS</td>
<td>Rutherford backscattering spectrometry</td>
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<td>rf</td>
<td>radio frequency</td>
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<td>R&lt;sub&gt;s&lt;/sub&gt;</td>
<td>sheet resistance</td>
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<td>secondary ion mass spectrometry</td>
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<td>tin oxide</td>
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<td>T</td>
<td>transmittance</td>
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<td>UV-Vis-NIR</td>
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<td>V&lt;sub&gt;OC&lt;/sub&gt;</td>
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CHAPTER 1
INTRODUCTION

Cadmium telluride (CdTe) solar cells are photovoltaic (PV) devices that harvest photons to produce useful electrical power. They are the leading thin-film PV technology, with primary commercialization through First Solar. Over 10 GW of CdTe modules have been fabricated to date with manufacturing costs as low as ~$0.65/W [1, 2]. Nearly all deployment has come in the form of utility-scale “solar farms” where CdTe PV’s low cost of energy is competitive with crystalline silicon (c-Si) PV, the industry leader. Further improvements in efficiency and/or cost reductions are required to meet the goals of the U.S. Department of Energy SunShot Initiative—$1.00/W installed by 2020 [3]—and compete with c-Si PV, wind, and fossil fuels.

Due to its optoelectronic properties, CdTe is a near-ideal photovoltaic absorber. Its 1.44 eV direct band gap is near-optimal for theoretical cell efficiency [4]. With an absorption coefficient greater than $1 \times 10^4$ cm$^{-1}$, a 2-µm thick layer absorbs 99% of incident sunlight at wavelengths less than 860 nm [5, 6]. However, low minority carrier lifetime and acceptor density are severe limitations in devices. Doping is thermodynamically unfavorable in $p$-type CdTe. Intrinsic doping, through interstitial, vacancy, or anti-site defects, is very low. CdTe congruently sublimes and condenses such that the vapor pressure of Cd atoms is twice that of Te$_2$ molecules and off-stoichiometry is limited to $\sim 1 \times 10^{-5}$ at. % in the growth temperature range 400–700 °C [7]. Extrinsic doping, through defects with foreign atoms, is limited by low dopant solubility, high activation energy, and/or unfavorable defect energy level [8]. Compensation of intrinsic and extrinsic dopants further limits the doping density [9]. Other layers in the device further limit performance, as will be discussed below.
Figure 1-1 displays the superstrate cell architecture that is most commonly employed. Glass is commonly used due to its high transparency and compatibility with high temperature processing. A transparent conductive oxide (TCO) is deposited directly on the glass to serve as the front electrical contact. Next, the high resistivity and transparent (HRT) buffer layer provides an electrical barrier between the TCO and CdTe layers. The most prevalent TCO/HRT combination is fluorine-doped and intrinsic tin oxide (FTO/TO), whereas the cadmium stannate/zinc stannate (CTO/ZTO) bilayer is a well-established alternative. An $n$-type cadmium sulfide (CdS) window layer forms a $pn$ junction with the $p$-type CdTe absorber. Last, one or more metallization films provide a back contact. Section 2-3 provides additional process-related information for devices made in this work. Sunlight must pass through the glass/TCO/HRT/window layers to contribute to the device output, because nearly all electron-hole pairs are generated via absorption in the CdTe layer. Photo-generated electrons and holes must move to the TCO and back contact, respectively, to be collected.

After plateauing at 16.7% for a decade, large research efforts at General Electric and First Solar have enabled significant device efficiency gains in the last five years. Record cell and module efficiencies are currently 21.5% and 18.6%, respectively [10, 11]. Table 1-1 compares the performance of the last six champion cells.

Efficiency $\eta$ is given by

$$\eta = \frac{J_{SC}V_{OC}FF}{P_{illumination}}$$

(1-1)

where $J_{SC}$ is the short-circuit current density in units of mA/cm$^2$, $V_{OC}$ is the open-circuit voltage in V, FF is the fill factor in percent, and $P_{illumination}$ is the power supplied by illumination in mW/cm$^2$. Section 2-4 further describes these parameters in the context of current-voltage measurement. For now, they may be qualitatively considered in terms of amount of collection.
Figure 1-1: CdTe solar cell layers for the superstrate architecture. Common layer materials are given in parentheses. FTO, CTO, TO, ZTO, CdS:O, ZnTe:Cu, Ti, Cu, and Au refer to fluorine-doped tin oxide, cadmium stannate, tin oxide, zinc stannate, oxygenated cadmium sulfide, copper-doped zinc telluride, titanium, copper, and gold, respectively.

\( J_{SC} \), junction-created electrical potential \( (V_{OC}) \), and overall diode quality \( (FF) \). The theoretical limits for individual CdTe devices under 1 sun illumination are \( J_{SC} = 30.5 \) mA/cm\(^2\), \( V_{OC} = 1.065 \) V, and \( FF = 88.6\% \), which would yield a 28.8% efficient device \[12\]. Note that the most recent champion cell has a \( J_{SC} \) higher than the theoretical limit due to band gap grading of the absorber layer. A majority of the \( \eta \) gains from the 2001 National Renewable Energy Laboratory (NREL) cell to the current record (25.7% relative improvement) have come from boosts in \( J_{SC} \) (15.9% improvement) rather than gains in \( V_{OC} \) (3.7% improvement) or \( FF \) (5.2% improvement). The overwhelming dependence on \( J_{SC} \) for efficiency gains suggests that it may be simpler in practice to maximize photon flux to and carrier generation in the CdTe layer than improve CdTe material quality through increased doping and/or lifetime.
Table 1-1: Solar cell parameters for the last six champion cells.

<table>
<thead>
<tr>
<th>Maker</th>
<th>Year</th>
<th>η (%)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NREL</td>
<td>2001</td>
<td>16.7</td>
<td>26.1</td>
<td>0.845</td>
<td>75.5</td>
<td>[13]</td>
</tr>
<tr>
<td>First Solar</td>
<td>2011</td>
<td>17.3</td>
<td>27.20*</td>
<td>0.842</td>
<td>75.6</td>
<td>[14]</td>
</tr>
<tr>
<td>General Electric</td>
<td>2012</td>
<td>18.3</td>
<td>26.95</td>
<td>0.857</td>
<td>77.0</td>
<td>[15]</td>
</tr>
<tr>
<td>First Solar</td>
<td>2013</td>
<td>19.6</td>
<td>28.59</td>
<td>0.857</td>
<td>80.0</td>
<td>[16]</td>
</tr>
<tr>
<td>First Solar</td>
<td>2014</td>
<td>21.0</td>
<td>30.25</td>
<td>0.875</td>
<td>79.4</td>
<td>[17]</td>
</tr>
<tr>
<td>First Solar</td>
<td>2015</td>
<td>21.5†</td>
<td>30.94</td>
<td>0.877</td>
<td>79.2</td>
<td>[10]</td>
</tr>
</tbody>
</table>

*Reported value was erroneous and has been corrected here.
†Device area less than 1 cm$^2$.

1.1 Advanced Front Contacts in CdTe Solar Cells

The processing and materials science of the front contact layers in CdTe solar cells is the focus of this thesis. Here, the front contacts are broadly defined as the layers supporting electron transport from the active CdTe layer to the external load: the TCO, HRT, and CdS window layers. HRT layer development is not a significant part of this work. The TCO layer has two primary requirements in the device. It should be optically transparent to minimize light attenuation and electrically conductive to minimize electrical losses. TCO materials have very low absorption in the visible and near-infrared (NIR) due to their wide band gap $>3$ eV.

Measurement of wavelength-dependent transmission, reflection, and absorption by spectrophotometry is discussed in Section 2.2. Simple and rapid determination of a thickness-dependent measure of film electrical resistance, the sheet resistance ($R_s$), is described in Section 2.3. Whereas films can be simply compared based on optical and electrical properties separately, a figure of merit $Φ$ is often used to evaluate their combined electrical and optical qualities. One such value is given by

$$Φ = \frac{T^{10}}{R_s}$$  \hspace{1cm} (1-2)
where $T$ is the transmittance and $R_s$ is the sheet resistance [18]. The value for $\Phi$ is generally a good predictor of TCO performance when incorporated in a device. Additional properties, such as chemical and thermal stability and mechanical adhesion to glass and HRT, should also be considered [19].

The two primary TCO materials for CdTe solar cells are fluorine-doped tin oxide (FTO) and cadmium stannate (CTO). FTO is used in commercial glass coated products for architectural and electronics applications. It is typically deposited at commercial scale by atmospheric pressure chemical vapor deposition (APCVD) at elevated temperature [20]. Newly-formed glass is coated downstream of the float line to reduce cost through energy savings. CTO, on the other hand, is a pre-commercial material that is deposited by sputtering [21], spray pyrolysis [22], metal-organic chemical vapor deposition [23], and dip-coating [24]. CTO has demonstrated superior performance compared to FTO based on higher conductivity and transmittance. For films with the same sheet resistance, CTO has far greater transparency and absorbs 75% less light than FTO [25]. Figure 1-2 shows the film transmittance for FTO and CTO films with $R_s \sim 12 \, \Omega$/sq. In the essential 400–860 nm wavelength range, the FTO transmits less than 80% whereas the CTO transmits greater than 85% of incident light. Higher electron mobility in CTO films is responsible for its improved electro-optical performance relative to FTO.

Despite its improved performance, CTO has not displaced FTO in commercial devices. Unlike FTO, which displays high performance as-deposited, room temperature-deposited CTO from a pre-reacted target requires a subsequent anneal in the presence of cadmium for optimum opto-electrical performance. Other strategies, such as reactive DC sputtering from a metallic Cd-Sn target [26], co-sputtering of CdO and SnO$_2$ [27], and high temperature sputter deposition [28], have been developed to eliminate the annealing step although the resulting films are
Figure 1-2: Comparison of film transmittance for FTO and CTO films. The $R_s$ for each film is $\sim 12 \, \Omega$/sq. Typically less conductive and/or have a reduced optical band gap. At the laboratory scale, the CTO anneal is often performed at 600–700 °C in the configuration shown in Figure 1-3. This process is termed the “proximity anneal”, in which a secondary CdS film is placed in contact with the CTO film. The films are placed between two graphite susceptors. Thermocouples placed in wells in the susceptors provide a feedback loop to the infrared (IR) lamps. The proximity anneal is used to dramatically increase transparency and electrical conductivity via recrystallization and a shift in composition.

The other important layer for these studies is the CdS window layer. In addition to its role as the $n$-type partner to CdTe, it must fulfill other requirements for optimal performance. First, the CdS should have a $\sim 1000$-fold higher carrier concentration than CdTe such that a large majority of the depletion region is in the CdTe layer. Next, the window layer must form a high-quality material and electrical junction with CdTe. The CdS/CdTe interface should have low
Figure 1-3: Schematic of the CTO proximity anneal.

defect density and the conduction band offset should be less than about 0.5 eV to allow adequate electron transport. Optically, the window layer must transmit light to the absorber layer. Unlike the wide band gap TCO, CdS has a band gap of ~2.4 eV. This results in absorption at wavelengths less than ~520 nm. CdS is a very good absorber, with an absorption coefficient ~5×10^4 cm⁻¹, but generated electron-hole pairs are lost via recombination due to low mobility [29]. Figure 1-4 illustrates the detrimental effect of parasitic CdS absorption on carrier collection. Incident photons with wavelengths in the yellow region may be uselessly absorbed by the lossy CdS in place of the intended CdTe layer. Unfortunately, the spectral range from 300–520 nm contains about 23% of the total AM1.5G spectrum available to CdTe [30]. The simplest strategy for reducing CdS absorption is to reduce the layer thickness. However, for CdS thicknesses <60 nm, the gains in J_{SC} are accompanied by losses in V_{OC} and FF due to space-charge imbalance and shunting [31].
Figure 1-4: AM1.5G solar spectrum. The yellow area indicates the spectral range where CdS parasitically absorbs some of the photon flux. The gray area indicates the range where a very high fraction of photons should reach the CdTe layer for collection.

CdS is typically deposited by evaporation [32], sputtering [33], close-space sublimation [34], or chemical bath deposition (CBD) [35]. Of these, CBD and sputtering are the most common. CBD is a solution-based technique featuring heterogeneous growth at moderate temperature. One common recipe consists of a stirred bath mixture of cadmium acetate, ammonium acetate, and ammonia at pH 13. Growth proceeds once limiting reagent thiourea is added to the bath maintained at 90 °C [36]. The primary stated advantage for CBD is low capital cost compared to vacuum-based techniques [37]. Meanwhile, sputtering has a number of compelling advantages. It is a well-known technique that is scalable, vacuum-based, and generates little or no liquid cadmium-containing waste. Several process parameters can be manipulated to alter film properties directly and systematically. For example, the sputter ambient composition is a powerful processing knob. Compared to films sputtered in pure argon,
those sputtered in an oxygen/argon mixed ambient have a higher optical band gap and exhibit reduced crystallinity [38]. These oxygenated CdS films are designated CdS:O. With a higher optical band gap, use of CdS:O in place of CdS should increase collection in the CdTe layer by narrowing the spectral range for window layer absorption (increasing the gray region in Figure 1-2 at the expense of the yellow region).

1.2 CdS/CdTe Interdiffusion

CdS appears at first to be a poor window layer and heteropartner for CdTe. Not only does CdS attenuate incident light, it also has a 9% lattice mismatch with CdTe. When CdTe is deposited directly on CdS, it may form a stressed layer with the same orientation as CdS (if at low temperature) [39] or form a randomly oriented layer accompanied by a large interface defect density [40]. CdS/CdTe interdiffusion partially alleviates these issues during high temperature CdTe deposition and cadmium chloride (CdCl₂) annealing processes. Diffusion is thought to occur by grain boundary and bulk diffusion, either during growth when CdTe is deposited at >500 °C [41] or during post-deposition CdCl₂ annealing when using lower temperature growth [42]. Chemical activation is essential, as thermal activation alone is less effective. Both diffusion mechanisms are influenced by CdCl₂ annealing ambient, and increase with increasing temperature and O₂ and CdCl₂ partial pressures [6, 43]. On the other hand, oxygen in the CdS film or CdTe growth ambient is thought to reduce sulfur and tellurium diffusion greatly [29, 38]. Yan and coworkers asserted that oxygen from the CdTe growth ambient migrates to CdTe grain boundaries, where it effectively hinders sulfur grain boundary diffusion [44].

Interdiffusion causes several alterations to the device. First, it leads to partial or complete consumption of the CdS layer. While device J_{SC} tends to increase as a result, excessive thinning may cause CdTe-TCO shunt pathways, which greatly reduce V_{OC} and FF. Also, interdiffusion
may form graded layers or alloys at or near the upper stability limits depending on processing conditions. The alloys $\text{CdS}_{1-y}\text{Te}_y$ and $\text{CdTe}_{1-x}\text{S}_x$ exhibit interesting optical and structural properties. The band gap $E_g$ of $\text{CdTe}_{1-x}\text{S}_x$ follows the bowing relation

$$E_g(x) = 2.4x + 1.51(1 - x) - bx(1 - x)$$

where $b$, the bowing parameter, is equal to 1.8 [45]. Thus, the CdTe layer has a lower band gap for $0 < x < 0.5$ and the CdS layer band gap is lower for any amount of Te alloying. Sulfur enrichment and tellurium deficiency in the CdTe layer potentially increase $J_{SC}$ by extending the spectral range for collection, whereas sulfur deficiency and tellurium enrichment in the CdS layer would effectively limit $J_{SC}$ by increasing the spectral range for parasitic absorption. The thermodynamic concentration limits are ~6 at. % sulfur in CdTe and ~3 at. % tellurium in CdS at CdCl$_2$ annealing temperature [43]. Structurally, the alloys follow Vegard’s rule [43]. For $\text{CdTe}_{1-x}\text{S}_x$, this is $x = 1.508(6.481 - a_0)$, where $a_0$ is the lattice parameter. By reducing interfacial lattice mismatch, alloy formation is believed to reduce defect formation at the junction [40].

### 1.3 Flexible Solar Cells

Thin-film PV devices have traditionally utilized a rigid glass substrate/superstrate to act as a handle during processing and as a protective barrier in deployment. Flexible glass offers several advantages, including weight reduction, deployment flexibility, and processing versatility. A National Science Foundation workshop panel concluded that the substitution of thin (<200 µm) flexible glass for thick (<1 mm) glass “would be nothing short of revolutionary” [46]. The flexible glass is wound on rolls at the glass manufacturer site. Device manufacturing then proceeds via roll-to-roll processing (R2R), in which the roll is continuously unwound upstream of the deposition sequence. Low temperature metal and oxide coatings on foils and plastics are commonly performed by R2R, although its application to high temperature
deposition and glass rolls is less well developed. R2R processing on flexible glass enables higher throughput manufacturing and reduced handling costs compared to processing on discrete sheets of rigid glass.

1.4 Outline of Thesis Goals

As described above, most of the recent gains in champion cell efficiency have come through improvements developed in corporate laboratories. These advances made by teams of researchers at one of two companies are now trade secrets or are vaguely described in the patent literature. The current champion cell is 4.3% absolute (25.7% relative) better than any certified cell a public research institution has made. The goal for researchers in the public domain should be to make advances that are useful to commercially successful CdTe enterprises and significantly advance public understanding of the underlying physics, chemistry, and materials science in these devices. R2R processing of devices on flexible glass could provide disruptive advances that improve performance and reduce operating costs. In order to improve the appeal of R2R processing, process development and high performance is required. This thesis seeks to develop processes for advanced front contact materials that are compatible with R2R processing on flexible glass and increase the materials science understanding of these materials.

The first goal was to develop enough understanding of the CTO fabrication steps to develop alternative sputtering/annealing processes amenable to scale-up and R2R processing that can replace or eliminate the proximity anneal, which requires a secondary consumable film and film-to-film contact. Alternative processes should reduce complications, have a wide processing window, and maintain or improve film performance. Chapter 3 describes the development of alternative processing schemes, compares resulting CTO performance, deduces the aspects of the
proximity anneal that make it effective, and explains the relative opto-electrical performance in the context of the underlying material science.

Next, a process for rf magnetron sputtering of CdS:O was developed as an alternative to CBD deposition. The goals were to gain understanding of important CdS:O properties and correlate them to device performance. More than simply prescribing the processing conditions used in fabricating the highest efficiency cell, the results are interpreted in terms of CdS:O optical band gap, composition, and bonding states. From target changes and process scale-up, the optical band gap appears to be a sufficient transferability metric whereas process conditions such as the sputter ambient composition are not. Chapter 4 outlines the effects of sputter ambient composition on CdS:O properties, trends between those properties and CdTe device results, and successful attempts in scaling up the process to larger deposition systems.

Last, two novel techniques were developed to enable characterization of the window layer in completed devices. The goals of this work were to understand how high temperature processing during CdTe device fabrication affects CdS:O properties and determine whether the degree of oxygenation affects CdS/CdTe interdiffusion. Examination of the window layer after cell fabrication is complicated by its thickness and position in the device. It is sandwiched between the glass/TCO/HRT layers on the front side and the CdTe/back contact layers on the back. At less than 100 nm in a device consisting of more than 5 µm of films, it is difficult to characterize through cross-sectional microscopy except via transmission electron microscopy (TEM). Two novel techniques were developed to enable simpler, and in some cases safer, characterization of the window layer and junction region. Chapter 5 describes the techniques and assesses their ability to expose the CdS layer in fabricated devices. The techniques were used to enable characterization in completed devices as well as glass/CdS/CdTe test structures,
each of which provides distinct advantages. Application on completed devices allows correlation between reasonable quality cells and characterization data, whereas additional processing options are available when using test structures.
CHAPTER 2
MATERIALS AND METHODS

In this chapter the experimental deposition systems and processes as well as the characterization methods employed in this thesis are described. The goal of this chapter is to provide an in-depth review of these techniques, whereas the subsequent chapters provide general descriptions relevant to the specific experiments employed. First, radio frequency magnetron sputtering is discussed, including details of the three sputter deposition systems used in this work. Next, relevant thin-film characterization methods are explained. Last, additional CdTe solar cell fabrication deposition processes and characterization methods are presented.

2.1 Radio Frequency Magnetron Sputtering

Sputtering is a thin-film physical vapor deposition (PVD) technique performed under vacuum [47, 48]. Typical applications include metallic [49, 50], ceramic [51, 52], and polymeric [53, 54] coatings. During sputtering, a plasma creates energetic electrons and ions that impinge upon a target, ejecting particles which condense on a substrate, forming a film. These sputtered particles may further react with the ambient either in the gas phase or upon deposition. This work employed ceramic targets, which are comprised of compounds that have been thermo-mechanically pressed into a high-density disc.

High-energy ions are created by setting a bias between the target (cathode) and substrate (anode) which creates a plasma through a cascade of electron impact ionization reactions. In the case of argon, the reaction proceeds via

\[ e^- + Ar \rightarrow 2e^- + Ar^+ \] (2-1)

where \( e^- \) is an electron, \( Ar \) is a neutral argon atom, and \( Ar^+ \) is a positively charged argon ion.
The ions thus formed are propelled by the electric field toward the target. Impingement at the target neutralizes the ions and causes a cascade of vibrations in the uppermost monolayers of the target surface. When the vibrational energy between atoms/molecules exceeds that of the binding energy, atoms/molecules leave the target surface and are said to be “sputtered”.

Sputtered particles typically have a mean free path of ~1 cm while the target-to-substrate distance is ~5 cm. Strictly speaking, free molecular flow conditions are not met because the sputtered particles statistically have a high probability of multiple collisions before deposition on the substrate. Even so, the film growth distribution is much closer to the cosine distribution in free molecular flow than continuum flow.

Radio frequency (rf) magnetron sputtering is a variation of the original direct current (DC) process, providing additional process flexibility at the expense of deposition rate. Most notably, rf magnetron sputtering enables the use of an insulating target [55]. The electrodes are biased using 13.56 MHz alternating current (AC) power. The high frequency switching has different effects on the ions and electrons. Large ions cannot react quickly enough to the high frequency signal. Instead, they respond solely to the DC bias (mean of the AC signal). Electrons are affected by the AC field, oscillating toward and away from the target. Contact between electrons and the target neutralizes positive charges on the target surface, thereby reducing Ar repulsion.

In magnetron sputtering, magnets are used to increase the plasma density in front of the target. Oppositely polarized magnets are placed behind the target. One common configuration is to arrange a disk-shaped magnet in the annulus of a second ring-shaped one. The resulting magnetic field parallel to the target induces an electrical field normal to the target, effectively increasing the electron residence time near the target. Electron impact ionization is much more
probable. The net effects are greater ionization efficiency of the ambient gas and fewer electrons impacting the substrate.

Figure 2-1 displays a schematic of the rf magnetron sputtering process. Electrons (red circles) have a large residence time near the target because of the magnetron-induced magnetic fields. Ar atoms (green circles) move by diffusion, randomly striking surfaces and other particles. The left side of the schematic represents the process when the target is at a high negative potential, whereas the right side represents the low negative potential condition. During the former, Ar atoms undergo electron impact ionization during collisions with electrons to form Ar ions and secondary electrons. Ar ions formed by electron impact ionization are attracted to the target by the induced electric field. Collision at the surface allows the positive charge to be transferred to the surface and sputters target material toward the substrate. On the right side, the target is at or near its lowest negative potential and fixed positive charges are present on the target surface. No sputtering takes place because the Ar ions are repelled from the target surface. Electrons recombine with the positive charges on the target, preparing it for sputtering during the next cycle.

rf sputtering utilizes capacitive power coupling. A matching network is used to match the power supply impedance in order to minimize reflected power. Figure 2-2 shows a simplified circuit diagram of the rf power supply, matching network, and sputtering chamber. The matching network is a modified L circuit consisting of fixed inductors and variable capacitors. The capacitance in series (C_Tune) and in parallel (C_Load) with the chamber are altered such that the combined impedances of the matching network and chamber equal the power supply impedance—typically 50 Ω.
Figure 2-1: Schematic depiction of rf magnetron sputtering using an argon ambient. The effects of AC switching are shown on the left side when the signal is negative and on the right side when the signal is positive. Green, red, and orange circles represent Ar atoms/ions, electrons, and the target material, respectively. The curved black lines represent the magnetic field caused by the oppositely polarized magnets below the target.

Figure 2-2: Simplified circuit diagram of the rf power supply, matching network, and sputtering chamber.
The ambient gas composition often has a large effect on the deposition rate and film composition. Sputtering in an inert ambient typically results in a high deposition rate and few reactions between the ambient and target material, although inert atoms can become trapped in the growing film [56]. In reactive sputtering, reactive gases are used to deposit films with different compositions than the target. For example, TiO$_2$ is commonly deposited from a Ti target in an oxygen-containing ambient. Reactive sputtering generally enables higher deposition rates than sputtering from a ceramic target. Electron impact ionization reactions form radicals, cations, and anions that subsequently undergo gas- and solid-phase reactions with the target material while in flight or at the target/substrate film surface. In this work, inert argon and reactive oxygen gas were used. The ambient compositions are given as the flow rate percentage of reactive O$_2$:

$$\% O_2 = \frac{F_{O_2}}{F_{Ar} + F_{O_2}} \times 100\%$$

where $F_{O_2}$ and $F_{Ar}$ are the flow rates of O$_2$ and Ar, respectively.

### 2.1.1 CVC SC-3000 sputter tool

The CVC SC-3000 is a single-source diffusion-pumped bell jar system used to deposit cadmium stannate (CTO) and oxygenated cadmium sulfide (CdS:O) in this work. Figure 2-3 shows a front-view of the system. The chamber exterior consists of an 18-in diameter × 30-in tall glass bell jar top and feedthrough collar, which is vacuum-sealed using a rubber gasket connected to the bell jar. The bell jar is suspended ~2 ft above the collar between runs and during chamber maintenance. A single 2-in sputter gun (US’ Gun II model SU-500-H) directly faces the substrate in sputter-up configuration. The gun is water-cooled to prevent thermal-induced shock and cracking of the target. The substrate holder is fixtures to the system by securing four corner screws through the holder and into a square metal block. The substrate
temperature is not controlled. A hand-operated shutter parallel to the target and substrate is used to block sputtered particles during pre-sputtering. Ambient gases Ar and O$_2$ are plumbed into the side of the bottom section and controlled by mass flow controllers (MFCs; MKS Instruments Type 1179A). There is a single 100 sccm MFC for Ar and two MFCs (10 and 100 sccm) for O$_2$ which are controlled independently using an MKS Type 247 four-channel readout. The ultimate pressure of this system was $\sim 2\times 10^{-7}$ Torr.

**Figure 2-3:** Schematic of the CVC SC-3000 sputter system.

As shown in Figure 2-3, the chamber is separately connected to a diffusion pump (CVC PVMS-100), for achieving high vacuum, and a mechanical pump (Edwards Model E2M40
PFPE), for rough pumping as well as backing the diffusion pump. The valves between the roughing pump and chamber (roughing valve) and between the roughing pump and diffusion pump (foreline valve) are electronically controlled. Meanwhile, the valve between the diffusion pump and chamber (gate valve) is hand-operated. A liquid N\textsubscript{2} cold trap was placed between the diffusion pump and gate valve to reduce pump oil backflow into the chamber. The unit is equipped with several pressure gauges. A Pirani gauge (Granville-Phillips Series 275 Convectron) measures chamber pressure from atmosphere (~6×10\textsuperscript{2} Torr) to 1×10\textsuperscript{-4} Torr, although the analog gauge controller has greatest utility >1 Torr. A capacitance manometer gauge (MKS Baratron Type 626A) is used to determine when the crossover pressure (~100 mTorr) is reached and in setting the ambient gas pressure. A wide range ion gauge (Varian type 564) is used for high vacuum measurement. Next to the substrate holder, a quartz crystal monitor (QCM; Inficon XTC) utilizing a 6 MHz gold crystal (thinfilmsupply.com Part ASC-010G) is used to calibrate the deposition rate. An rf power supply (Advanced Energy RFX 600A) hooked up to the sputter gun provides up to 1000 W. Matching is provided by an RF Plasma Products Model AM-5 unit. A general deposition procedure is provided in Appendix B.1. Most operations are performed manually in this system, with the exception of opening/closing the vent, roughing, foreline, and MFC valves.

Film thickness uniformity was a concern in this system, because the substrate is not rotated and is parallel to the target. Thickness was measured every 3 mm over the middle 27 mm in two axes normal to the substrate sides of a 1.5-in × 1.5-in substrate. This area was selected because it matches the extent of solar cell boundaries (see Section 2.3.6). Figure 2-4 shows the thickness uniformity for a ~100 nm CdS film. As expected, maximum thickness is observed
near the center of the substrate. Deviation from the average thickness was less than ±10% for nearly all scanned points.

![Graph showing thickness uniformity of a CVC-deposited CdS film. The nominal film thickness was 100 nm.](image)

**Figure 2-4:** Thickness uniformity of a CVC-deposited CdS film. The nominal film thickness was 100 nm.

### 2.1.2 Kurt J. Lesker CMS 18 sputter tool

The Kurt J. Lesker (KJL) CMS 18 is a turbo-pumped four-source system equipped with a load lock, as shown in Figure 2-5. CTO and CdS:O films were deposited in this system. This system has several advantages over the CVC tool described in the previous section. The use of larger substrates (either one 3-in × 3-in or four 1.5-in × 1.5-in) and a load lock greatly increases throughput. In some cases, even greater gains were achieved when multiple sputter sources were used consecutively on the same substrate. Far better base pressure (~1×10⁻⁷ Torr) and ultimate pressure (2×10⁻⁸ Torr) are reached in this system. Most actions, such as pumping, venting, loading/unloading of substrates, and depositions were performed using automated
recipes in KJL’s proprietary software. The automated recipes are created in a line by line manner using an MS Access-based program.

The main chamber has a 24-in diameter and is 15 in tall with a horizontal O ring-sealed flange. The top portion is hoisted and rotated off-axis during maintenance work. Four 3-in KJL Torus guns are positioned in sputter-up configuration in a confocal pattern at roughly the same separation distance from the substrate. The substrate is rotated during deposition to improve uniformity. A substrate shutter and individual sputter target shutters are pneumatically actuated. Cross-contamination between targets was minimized using shutters for each source and extended pre-sputtering for 5–10 min. In some cases, visible contamination on target surfaces was removed by manual scrubbing using a Scotch-Brite pad (3M) during target changes/chamber maintenance. Gases Ar and O₂ are plumbed into the system and controlled via two MFCs (MKS Mass-Flo 1179A), with ranges of 10 and 100 sccm for each.

Figure 2-5: Schematic of the Kurt J. Lesker CMS-18 system.
A Shimadzu TMP-1003 LM turbomolecular pump is mounted horizontally to the chamber using a 10-in Conflat flange. A variable position gate valve between the turbo pump and chamber allows pump isolation and downstream operation. The load lock, positioned 180° from the chamber pump, is evacuated using a BOC Edwards EXT 70H turbomolecular pump. Both turbo pumps are backed by the same mechanical pump (BOC Edwards RV12F). Valves between each turbo pump and their convergence allowed independent rough pumping and backing of either the chamber and Shimadzu pump or load lock and BOC Edwards pump. High and low vacuum pressures in the chamber and load lock are measured using ion gauges (KJL Part G100F) and wide range Convectron gauges (Granville-Phillips Type 275). Deposition pressures were measured using a capacitance manometer (MKS Baratron Type 627B). The rf power supply and matching network are KJL R601 and KJL MC2 units, respectively.

2.1.3 Unifilm PVD-300 sputter tool

The Unifilm PVD-300 is a cryogenic-pumped multi-source system equipped with a load lock. Figure 2-6 shows a schematic of the system. This system was used to deposit CdS:O and copper-doped zinc telluride (ZnTe:Cu) films and for ion beam milling of CdTe back surfaces and back contacts. This system has several advantages over the CVC tool described in Section 2.1.1. The use of larger substrates (either one 3-in × 3-in or four 1.5-in × 1.5-in) and a load lock greatly increases productivity. Far better base pressure (~1×10⁻⁷ Torr) and ultimate pressure (~9×10⁻⁸ Torr) are reached in this system. Operations were performed using Unifilm’s graphical user interface and recipe builder. The chamber is a 25-in diameter × 8-in height cylinder with a horizontal O ring-sealed flange. The top section is mounted to a motor for opening during chamber maintenance. A set of round planets are arranged in a circular pattern on a rotating base. These planets are used to support the substrate platen and rotate during deposition. The
chamber is currently equipped with two rf sputter sources (2-in and 3-in KJL Torus guns), one DC sputter source (Sloan SC-10), and an ion gun (Ion Tech, Inc. Model 3.0-1500-100) mounted to the chamber lid. Ambient gases Ar and O$_2$ are plumbed to the system and controlled using MKS Mass-Flo Type 1179A MFCs with ranges of 100 and 10 sccm, respectively.

A Varian Type 564 wide range ion gauge is used at high vacuum. A capacitance manometer (MKS Baratron Type 690A) measured chamber pressure during the deposition. rf power was supplied by an RF Plasma Products Inc. RF 10S and matched using an RF Plasma Products Inc. Model AM-10. The DC power supply is an Electronic Measurements, Inc. Model 600S4.5-2-D-0335. The mechanical pump (Leybold Trivac A) is used to rough the load lock and chamber. A cryogenic pump (CTI-Cryogenics Cryo-Torr 8) brings the chamber to high vacuum. Typical base pressures in the system were $\sim 1 \times 10^{-7}$ Torr.
2.1.4 Safety considerations for sputtering cadmium compounds

During deposition, a fraction of sputtered particles undesirably coat surfaces inside the chamber, including the chamber wall, substrate holder, and the target clamp ring. These coated surfaces present exposure hazards to users performing target changes or other maintenance activities inside the chamber. Macroscopic and microscopic flakes may peel off of these surfaces and come into contact with the user via inhalation and contact with the skin, mouth, or eyes. In the case of cadmium-containing compounds, these flakes may be carcinogenic and/or mutagenic. To mitigate these risks, users should wear gloves and eye protection at all times, and the chamber area should be well-ventilated. If sufficient ventilation is not available, the user should wear a half-face respirator.

2.2 Thin-Film Characterization Methods

The following techniques were used to characterize thin films.

2.2.1 Contact profilometry

Contact profilometry is a direct physical technique for measuring thickness. It is applicable to planar measurements from ~1 nm to ~500 µm. Prior to measurement, a step edge is created in the film using a masked etch or razor blade scratch. The Dektak 8 stylus profilometer (Veeco) was used for all such measurements. The vertical position of the stylus is recorded as it moves across the surface of the film. The raw data is adjusted to account for the stage slope. Most reported values were averaged over 3–5 measurements to minimize the effect of anomalies related to surface debris and imperfect step edges.

2.2.2 Spectroscopic ellipsometry

Spectroscopic ellipsometry is an indirect technique for measuring thickness. A source supplies polarized light to the material, while a detector measures the light output. An alpha-SE
(J.A. Woolam Co.) ellipsometer was used in this work. The polarity of the light is altered through interactions with the film. The changes in amplitude and phase are recorded as a function of wavelength. A model incorporating the index of refraction and thickness over the wavelength range is fit to the experimental data using regression. The thickness is determined by minimizing the mean squared error of the model fit.

### 2.2.3 UV-Vis-NIR spectrophotometry

Ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometry was used to measure the optical response of films. Cary 5000 and Cary 6000i (Varian) units were used. A monochromator with a variable grating filters the wide-spectrum lamp light into variable monochromatic light. Film transmittance and reflectance are determined at discrete wavelengths by detecting the fractions of total light transmitted through and reflected from the film, respectively. Integrating spheres installed in each system combine the specular and diffuse reflectance components. Absorbance was simply calculated as the balance fraction of light. Prior to measurement, baseline and zero scans were performed to correct for source and detector fluctuations.

One of the primary metrics calculated from the response is the optical band gap $E_g$. While there are several alternative methods [57], Tauc plot analysis was used in this work [58]. First, the absorption coefficient $\alpha$ was calculated using

$$
\alpha = \frac{1}{t} \ln \left[ \frac{100 - R}{T} \right]
$$

where $T$ is the transmittance and $R$ is the reflectance. Optical transitions in semiconductors follow

$$
(\alpha h\nu) = A(h\nu - E_g)^n
$$

(2-4)
where h is Planck’s constant, ν is the frequency, A is a proportionality constant, and n is an exponent whose value depends on the type of transition [58]. Values for n are 0.5 for direct and 1.5 for indirect transitions. \( E_g \) was determined as the x-intercept of an extrapolation of the linear portion of \((\alpha h \nu)^{1/n}\) versus \( h \nu \). The biggest source of uncertainty with this technique is the choice of y-axis scaling for linearizing the curve. Extracted values may be affected by band tailing at low scaling, yet they are often over-estimated compared to consensus values when scaling near the maximum values of the curve. In this work, the curves were linearized at \( 5 \times 10^9 \text{ eV}^2/\text{cm}^2 \), where extracted optical band gap values were very close to published ones. Figure 2-7 displays an example Tauc plot for cadmium stannate, which has a direct band gap.

\[\text{Figure 2-7: Example Tauc plot for the direct band gap determination of a cadmium stannate film.}\]
2.2.4 X-ray diffraction

Film crystallinity was determined by X-ray diffraction (XRD). Structures with crystalline or polycrystalline order diffract X-rays as a result of in-phase scattering. Figure 2-8 displays a schematic of the process. X-rays 1, 2, and 3 are incident at angle θ to atoms B, A, and D, respectively. Although the X-rays are scattered in all directions from the atoms, diffraction only occurs at an angle θ from the planes of atoms. This is a result of equal X-ray path lengths for X-rays 1 and 2, and of X-ray path lengths differing by the X-ray wavelength in the case of 1 and 2 compared to 3. The difference in path length for X-rays 1 and 3 is given by

\[ GD + DH = d\sin\theta + d\sin\theta = 2d\sin\theta \]  
\[ (2-5) \]

where d is the interatomic spacing. There is only constructive interference in the case where this difference is equal to a multiple of the X-ray wavelength. This condition is given by Bragg’s law:

\[ n\lambda = 2d\sin\theta \]  
\[ (2-6) \]

where n is an integer greater than zero and \( \lambda \) is the wavelength of X-ray radiation [59].

**Figure 2-8:** Schematic of X-ray diffraction by a crystal. Adapted from Cullity [60].
Both the Siemens Krystalloflex 810 at CSM and the Rigaku Ultima IV at NREL were used. The working principle for these diffractometers is the same. An X-ray source emits Cu Kα radiation at a wavelength of 1.5418 Å onto the film, while a detector counts incident radiation diffracted from the film. Two types of scans were performed. First, symmetric 0/2θ scans in which the source and detector are positioned at equal angles from horizontal. This type of scan is useful for phase identification and orientation determination. Also, glancing incidence 2θ scans were performed in which the source is fixed at a small angle. This type of scan is useful for phase identification and for probing the near-surface volume, and was used in this work to analyze thin-film layers while minimizing interference from underlying material.

2.2.5 Four-point probe and Hall system

Bulk and film electrical properties of the thin-film layers were measured by collinear four-point probe and Hall system. Material resistivity, the reciprocal of conductivity, is given by

\[ \rho = \frac{1}{ne\mu} \]  

(2-7)

where \( n \) is the carrier concentration (/cm³), \( e \) is the charge of an electron (1.6×10⁻¹⁹ C), and \( \mu \) is the mobility (cm²/V-s). As a bulk property, resistivity is typically thickness-independent. Its film property analog is sheet resistance \( R_s \), given by

\[ R_s = \frac{\rho}{t} \]  

(2-8)

where \( t \) is the film thickness. These measures of electrical transport are used differently in device design. Whereas \( \rho \) quantifies the overall resistance to current in a material, \( R_s \) is the resistance across the surface of a particular film. In TCO development for solar cells, the desired \( R_s \) (often ~10 Ω/sq [61]) sets the layer thickness for a material with a given \( \rho \) value. By lowering a material’s \( \rho \), the required thickness is decreased and the resulting transmittance through the
material is improved. Typically, it is more beneficial to minimize $\rho$ by increasing $\mu$ rather than $n$, because parasitic free carrier absorption is proportional to $n$.

A collinear four-point probe was used for quick and accurate $R_s$ measurement. Figure 2-9 displays a schematic of the measurement and important parameters [62]. The probes are spaced equally by a length $s$ along a film with thickness $t$, length $L$, and width $w$. The outer probe on the left side supplies current to the film at $x$ equal to 0 via a fixed current source. Current flows through the film and exits through the outer right probe. The two inner probes measure the potential difference along the path of current flow from $x_1$ to $x_2$.

\[ dR = \frac{\rho}{A} \, dx \]  

\textbf{Figure 2-9:} Schematic of the four-point probe measurement.

The differential resistance is given by

\[ dR = \frac{\rho}{A} \, dx \]  

where $A$ is the area of current flow. For thin films, this area is a cylinder with radius $x$ and height $t$. The resistance is given by
\[ R = \int_{x_1}^{x_2} \frac{\rho dx}{2\pi xt} \]  

(2-10)

where \( t \) is the film thickness. Because \( x_2 \) is two times larger than \( x_1 \), the result is

\[ R = \frac{\rho \ln(2)}{2\pi t} \]  

(2-11)

Finally, substitute \( R \) using Ohm’s law and use Equation (2-7) to obtain

\[ R_s = \left( \frac{\pi}{\ln(2)} \right) \left( \frac{V}{T} \right) \]  

(2-12)

which gives \( R_s \) in terms of the supplied current and measured voltage. It is important to note that this formula assumes that the probes are far away from the film boundary (\( L >> 3s, w >> s \)).

Correction factors for various non-ideal measurement geometries are given in [63].

Film resistivity, mobility, and carrier concentration were determined using the Hall effect. Films were cut into \( 1 \times 1 \text{ cm}^2 \) pieces. Indium wire was cut into small chunks and applied to the four corners of the film. The four probes of the Hall system (Bio-Rad HL5500PC) were contacted to these ohmic contacts in van der Pauw configuration [64]. Two checks were made prior to measurement. First, the resistance was measured for every probe combination. In cases where the maximum resistance was more than 150% greater than the minimum resistance, the probes and/or indium pads were re-contacted. Next, the current source was calibrated such that a desired voltage was produced. The software bounds were 4 to 100 mV, whereas the measurements were performed at 5, 10, and 20 mV in most cases. There were often small differences in obtained values at the different voltages, although there were no reproducible trends. Measurements at 10 mV are reported here.

First, \( R_s \) is measured using the van der Pauw method [64]. This step is performed to enable calculation of \( n \) and \( \mu \) during the final step. Current is applied between two contacts
while the voltage between the other two contacts is measured. This procedure is repeated for all combinations of probes. Film resistivity \( \rho \) is calculated via

\[
\rho = \frac{FQ\pi t}{2\ln(2)} (V_{ij} + V_{il})
\]

(2-13)

where \( F \) is a correction factor, \( Q \) is a symmetry factor, \( t \) is the film thickness, \( I \) is the constant current used for all measurements, and \( V_{ij} \) and \( V_{il} \) are voltages between contacts along the axes of the sample. The correction factor is calculated from

\[
F = 1 - 0.34657A - 0.09236A^2
\]

(2-14)

where \( A \) is a factor calculated using

\[
A = \left( \frac{Q - 1}{Q + 1} \right)^2
\]

(2-15)

and \( Q \) is given by

\[
Q = \frac{V_{ij}}{V_{il}}
\]

(2-16)

Finally, the Hall effect is used to calculate \( n \) and \( \mu \). Figure 2-10 displays the setup and effect of electrical and magnetic fields on the current path. A current source is connected to diagonal probes \( i \) and \( k \) while the opposite probes \( j \) and \( l \) are connected to a voltmeter. A fixed magnet supplies a constant magnetic field normal to the film plane. The current source directs current into the film via contact \( i \). The magnetic field induces an electrical field on carriers in the film. At steady-state, the Lorentz force equals 0 and the magnetic and electrostatic forces must be equal:

\[
v \times B = q \cdot E
\]

(2-17)

where \( v \) is the carrier velocity, \( B \) is the applied magnetic field, \( q \) is the electron charge, and \( E \) is the resulting electric field.
The Hall coefficient $R_H$ is calculated from

$$R_H = \frac{V_H t}{IB} \quad (2-18)$$

where $V_H$ is the Hall voltage. The carrier density and mobility are then calculated via

$$N = \frac{1}{qR_H} \quad (2-19)$$
$$\mu = \frac{R_H}{\rho} \quad (2-20)$$

### 2.2.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used for bonding state and composition determination. The sample is placed in a vacuum chamber that is subsequently pumped to $\sim 1 \times 10^{-9}$ Torr to ensure free molecular flow of particles. Figure 2-11 shows a schematic illustrating the emission of a carbon 1s electron by X-ray radiation. Monochromatic X-rays are focused on the material. Electrons absorbing X-ray radiation gain enough energy to exit the material. A detector and energy analyzer count and measure the kinetic energy of emitted electrons. Electrons are identified by their characteristic binding energy ($E_B$), which is given by
\[ E_B = E_{ph} - E_k - \Phi \]  

(2-21)

where \( E_{ph} \) is the X-ray energy, \( E_k \) is the kinetic energy of emitted electrons, and \( \Phi \) is the instrument-specific work function. Because the electron escape depth is only about \( \sim 10 \text{ Å} \), the technique is highly surface sensitive. Typically, an initial low-resolution survey scan is performed over a broad range of \( E_B \) prior to targeted high-resolution scans of specific constituents. High-resolution scans enable elemental quantification and analysis of binding states. Each type of electron, such as carbon 1s, has a characteristic \( E_B \) and relative sensitivity factor (RSF). To quantify, peak areas are divided by the RSF such that \( \sum_{i=1}^{n} \frac{\text{Peak Area}_i}{\text{RSF}_i} = 1 \), where \( n \) is the number of elements present in the material. Binding states are deduced by comparing high-resolution data to expected \( E_B \) ranges from references such as [65]. To take an example from Chapter 4, sulfide ions (\( S^{2-} \)) can be differentiated from oxygenated sulfur species (e.g. \( \text{SO}_3^{2-} \) and \( \text{SO}_4^{2-} \)) based on their characteristic binding energies. In this work, a Physical Electronics 5600 unit was used with Al radiation and pass energies of 187.85 and 11.75 eV for survey and high-resolution scans, respectively. CasaXPS software (Casa Software, Ltd.) was used to resolve and quantify the data.

2.2.7 Rutherford backscattering spectrometry

Rutherford backscattering spectrometry (RBS) was used to investigate the bulk chemical composition in films. Figure 2-12 displays the working principle of the technique. Light ions with mass \( m_i \) are accelerated toward the sample at a known energy \( E_i \). After colliding with sample atoms, ions scatter along a range of angles \( \theta \). In RBS, the detector is placed such that only ions with a scattering angle of \( \sim 150–175^\circ \) relative to the incoming axis are detected. The silicon solid-state diode detector translates the number of generated electron-hole pairs to ion energy.
Both the angle of scattering and the amount of energy transferred from the ion to the sample atom are governed by elastic collision. The cross-section of scattering at an angle θ, \( \sigma(\theta) \), is given by
\[ \sigma(\theta) = \left[ \frac{Z_i Z_s e^2}{4E_i [\sin(\theta/2)]^2} \right]^2 \]  

(2-22)

where \( Z_i \) and \( Z_s \) are the incident and sample atomic numbers, respectively. The energy of the backscattered ions \( E_{bs} \) is given by

\[ E_{bs} = \left( \frac{m_1 \cos(\theta) + \sqrt{m_2^2 - m_1^2 \sin^2(\theta)}}{m_1 + m_s} \right)^2 E_i \]  

(2-23)

where \( m_s \) is the mass of the sample atom [67]. Note that weaker inelastic scattering by the sample electrons causes energy broadening in RBS spectra, which can be used to estimate film thickness. In this work, a custom-built NEC unit was used [68]. The incident ions were \( \text{He}^+ \) energized to 2 MeV. The detector was positioned to receive backscattered ions at 169°. To quantify the relative atomic abundances, peak ratios were divided by the square of the atomic mass such that \( \int_1^n \frac{\text{Peak area}_i}{Z_i^2} = 1 \). The attenuation depth is much greater than the thickness of the films studied in this work. Silicon substrates were used to avoid peak interferences caused by glass.

2.3 Solar Cell Fabrication

This section describes the processes used for fabricating CdTe solar cells. Sub-sections proceed in the order of fabrication, using the device architecture shown in Figure 2-13.

2.3.1 Glass selection and cleaning

The choice of glass superstrate is non-trivial. The glass must have high optical transparency to minimize parasitic losses and thermal stability at CdTe deposition temperatures of \(-600 \, ^\circ\text{C}\). In addition, the coefficient of linear thermal expansion (CTE) should be close to that of CdTe (\(49 \times 10^{-7}/\text{K} \) at 300 K) to reduce stress formation. Corning 7059 alkali-free
**Figure 2-13:** CdTe solar cell architecture.

Borosilicate glass was used as the superstrate for devices presented in this work. It has been used in the fabrication of previous world record devices [25, 69]. This glass has high optical transmission (>90% in the CdTe spectral range), an annealing point >600 °C, and a well-matched CTE (46×10⁻⁷/K) [70]. Although 7059 production has been discontinued, 0.7 mm-thick pieces obtained from second-hand outlets were used as the superstrate for all devices reported in this work. An eventual replacement for 7059 will be necessary to utilize the high temperature (>500 °C) processing described here. Standalone films and test structures were fabricated on Corning Eagle XG glass. This glass remains in production and has better thermal stability than 7059.

The 3-in × 3-in glass pieces were cleaned to remove adsorbed particles and organics, which cause local non-uniformities in the device. The substrates were sonicated for at least 60 min in a heated 1 vol. % solution of Liquinox (Alconox, Inc.). An alternating pattern of rinses in two deionized water-filled 4-L beakers and 5-min heated sonication was repeated three times. A spin-rinse dryer was used to complete the cleaning. The glass was marked with a unique identifier using a diamond scribe and cleaved into 1.5-in × 1.5-in pieces to accommodate the close-space sublimation systems.
2.3.2 Transparent conductive oxide/high resistivity transparent oxide layers

As stated previously, the TCO layer provides a highly conductive contact to the front side of the cell, whereas the HRT layer blocks harmful TCO/CdTe shunt pathways. Both of these layers should be highly transparent for maximum collection. Two TCO/HRT layer combinations were considered in this work: FTO/TO and CTO/ZTO. A majority of the cells fabricated in this work incorporated the former, while Chapter 3 presents work on CTO.

2.3.2.1 Metal-organic chemical vapor deposited FTO/TO

Metal-organic chemical vapor deposition (MOCVD) was used to deposit fluorine-doped tin oxide (FTO) and tin oxide (TO) layers. Reactants tetramethyl tin (Air Products, 99.999% purity) and oxygen and carrier gas nitrogen enter the reactor. Reactants diffuse to and absorb on the surface, forming tin oxide at high temperature. The general reaction is

\[ \text{Sn(CH}_3\text{)}_4 + 8\text{O}_2 \rightarrow \text{SnO}_2 + 6\text{H}_2\text{O} + 4\text{CO}_2 \]  

(2-24)

Typical deposition temperatures were ~550 °C. For FTO deposition, bromotrifluoromethane (Matheson, 99.5% purity) is added as the fluorine precursor. Typical layer thicknesses in devices were 500 and 100 nm for FTO and TO, respectively. For additional reactor and process description, see [20].

2.3.2.2 Sputter deposited CTO/ZTO

Room temperature rf magnetron sputtering was used to deposit CTO and ZTO layers in the CVC SC-3000 and KJL CMS 18 tools described in Sections 2.1.1 and 2.1.2. The sputter targets were sourced from Materion Corp. Whereas the CTO target was formed from a pre-reacted mixture of CdO and SnO₂ in the same stoichiometric ratios as the film (i.e. 2:1 ratio of CdO:SnO₂), the ZTO target was a 1:2 mixture of ZnO and SnO₂. Pure O₂ or mixed O₂/Ar ambient gas compositions were used. The as-deposited films were annealed at 550–650 °C in a
close-space sublimation chamber using the configuration shown in Figure 1-3 or an alternative developed in Chapter 3. With a resistivity of ~2\times10^{-4} \, \Omega\cdot\text{cm}, the CTO layers were typically ~200 nm to provide 10 \, \Omega/\text{sq} material. The ZTO HRT layer is generally more difficult to characterize. Layer thicknesses of 25–150 nm were used.

2.3.3 CdS window layer

Two techniques were employed to deposit the window layer: CBD and sputtering. CBD development was mature prior to NREL’s success using sputtering processes, and many of the highest efficiency devices used CBD [25, 69, 71]. Sputtering has gained traction more recently due to scale-up considerations and demonstrated performance. Most of the devices fabricated in this work incorporated sputtered CdS:O layers.

2.3.3.1 Chemical bath deposited CdS

Up to six substrates were coated at a time using a hexagonal quartz fixture. The fixture contains a vertical support along each outer edge and a lower concentric hexagonal ring with lips on the inner edges. The substrates were placed at a ~20° angle from vertical with the device side facing inward. The bottom edge of each piece rests against a lip in the quartz fixture and the top edge rests against a vertical support. The fixture was placed into a stirred water-jacketed beaker containing 500 mL water and covered using Saran wrap. A temperature-controlled circulating water system was used to control the beaker temperature. The beaker was heated to 80 °C, at which time 8 mL of 0.033 M cadmium acetate (Cd(C_2H_3O_2)_2), 4.6 mL of 1 M ammonium acetate (NH_4C_2H_3O_2), and 15 mL of 15 M ammonium hydroxide (NH_4OH) were added to the beaker. Due to the high pH ~13, cadmium and ammonium ions bond in solution and undergo the reversible adsorption reaction given by

\[
\text{Cd(NH}_3)_4^{2+} + 2\text{OH}^- \leftrightarrow \text{Cd(OH)}_2 + 4\text{NH}_3
\]  

(2-25)
Next, the beaker was heated to 92 °C prior to addition of 8 mL of 0.067 M thiourea. A CdS complex forms on the surface via

\[
\text{Cd(OH)}_2 + \text{SC(NH}_2\text{)}_2 \rightarrow [\text{Cd(SC(NH}_2\text{)}_2)(\text{OH})_2]
\]  
(2-26)

Finally, the adsorbed complex is broken down through

\[
[Cd(\text{SC(NH}_2\text{)}_2)(\text{OH})_2] \rightarrow \text{CdS} + \text{CN}_2\text{H}_2 + 2\text{H}_2\text{O}
\]  
(2-27)

This heterogeneous reaction pathway was proposed by [72]. After 30 min, the fixture was removed from the beaker and placed in fresh deionize water. Because deposition occurs on both sides of the glass, cotton swabs saturated in hydrochloric acid were used to remove growth on the non-device side. Finally, the substrates were blown dry using N\text{}_2. For additional information on this process, see [36]. Film thickness uniformity was poor, varying between 40 and 130 nm on the same 1.5-in × 1.5-in substrate.

2.3.3.2 Sputter deposited CdS:O

Films were deposited at room temperature in the CVC SC-3000, KJL CMS 18, and Unifilm PVD-300 systems as outlined in Sections 2.1.1, 2.1.2, and 2.1.3, respectively. Pre-reacted CdS targets (Materion, 99.99% purity) were used. The ratio of O\text{}_2/\text{Ar} in the ambient greatly affects the film optical properties. Due to differences in pump types and plumbing geometry, the optimal ambient composition for device performance was determined for each system, as discussed in Chapter 4. The sputter power density was ~15 W/cm\text{\textsuperscript{2}}.

2.3.4 CdTe absorber layer

Close-spaced sublimation (CSS) processes were used to deposit CdTe films and perform CdCl\text{\textsubscript{2}} annealing steps. Sublimation is the physical transition from solid phase to gas phase without creation of an intermediate liquid phase. CdTe congruently sublimes such that the partial pressure of Cd is exactly twice that of Te\text{\textsubscript{2}} dimers. The as-deposited material displays low
efficiency in devices. Post-deposition annealing with liquid- or vapor-phase CdCl₂ has become a mainstay in device processing [73]. The anneal greatly improves device performance through trap passivation and \( p \)-type doping (e.g. \( V_{\text{Cd}} + \text{Cl}_{\text{Te}} \) complexes [8]), while it promotes CdTe recrystallization and CdS/CdTe interdiffusion [74]. An etch is used to remove impurities formed near the CdTe surface during the CdCl₂ anneal step [75].

2.3.4.1 Close-space sublimation deposited CdTe

CdTe films were deposited using intermediary source plates containing thick >100 µm films. The deposition assembly for source plate and CdTe film deposition steps are very similar. Source plates were fabricated as shown in Figure 2-14. CdTe powder purchased from Alfa Aesar (99.999% purity) was pulverized using a mortar and pestle. A 2-in × 2-in × 0.25-in pyrolytically coated graphite block (source susceptor) with a depression in one of the primary faces was filled with ~9 g CdTe. Two 0.5 cm × 0.5 cm × 4 cm quartz spacers were placed between the source susceptor and a clean piece of Corning 7059 glass. A second graphite susceptor (substrate) was placed directly on top of the source plate glass. Type K thermocouples were placed in holes drilled into the susceptors for temperature control. Two IR lamps (USHIO America, Inc.) above and below the assembly provided controlled heating. All pumping/venting, gas flow, and lamp power were controlled by a LabView program. After the initial chamber pumpdown, 20 Torr H₂ was introduced to the chamber. The source and substrate susceptors were heated to 700 and 600 °C, respectively, and held for 75 min. The deposition steps can be repeated up to two additional times to produce a total of three source plates from the original 9 g of pulverized powder.

CdTe films were deposited from CdTe source plates in a similar assembly. A second flat graphite block was substituted for the source susceptor while a CdTe source plate was placed in
parallel to a Glass/TCO/HRT/CdS device stack. The ambient was typically a 1:15 molar mixture of O\textsubscript{2} in He at 16 Torr. The source and substrate susceptors were heated to \~650 °C and 600 °C, respectively, and held for \~3 min such that the deposited film was 2–6 \textmu m. Typically, source plates were used for 10–15 CdTe film depositions and their use was discontinued once pinholes became visible.

Figure 2-14: Schematic of the close-spaced sublimation setup for CdTe source plate depositions from CdTe powder. Similar assemblies are used for CdTe film depositions from CdTe source plates and CdCl\textsubscript{2} anneals.

2.3.4.2 CdCl\textsubscript{2} anneal

The CdCl\textsubscript{2} anneal was performed on Glass/TCO/HRT/CdS/CdTe device stacks in a second close-space sublimation chamber in a similar assembly to the one shown in Figure 2-14. Analogous to the source susceptor fill described for source plate depositions, CdCl\textsubscript{2} crystallites (Alfa-Aesar, 99.998% purity) were placed in a depression in the source susceptor. The chamber was pumped down, then filled with a 1:4 mixture of O\textsubscript{2} in He at 400 Torr. The source and substrate susceptors were ramped up to 400 °C and held for 10 min.
2.3.4.3 CdTe etch

The back surface of the CdCl$_2$-annealed CdTe layer is commonly etched to remove contaminants prior to back contact deposition. Two etch processes were used in this work. First, an Ar ion beam etch was performed in the Unifilm system described in Section 2.1.3 when using a sputtered ZnTe:Cu/Ti back contact. The substrate was heated to ~320 °C prior to etching. The ion gun (Ion Tech, Inc. Model 3.0-1500-100) had a discharge voltage of 45 V, beam current of 6 mA, and beam voltage of 500 V. Etching was performed for 5 min with an estimated etch rate of 20 nm/min. The CdTe surface is thought to be near-stoichiometric after this etch. Alternatively, a liquid etch was performed for 20 s using a 0.05 vol. % solution of bromine in methanol when using an evaporated Cu/Au back contact. The bromine/methanol etch is believed to preferentially etch Cd [76]. The remaining tellurium-rich surface layer is believed to be more highly p-doped and therefore is more able to form an ohmic contact than bulk CdTe [77].

2.3.5 Back contact

Formation of an ohmic back contact to the CdTe absorber layer is notoriously difficult. A metal with a work function of ~5.7 eV is required to form a CdTe/metal contact without a barrier. No cost-effective metals satisfy this criterion, so alternative schemes are required. In this work, two pathways were used. First, a highly doped intermediate ZnTe:Cu layer was deposited between the CdTe layer and a Ti metallization layer. The ZnTe:Cu has much higher p-type doping than the CdTe layer, such that a lower work function metal can form an ohmic contact to it [78]. Alternatively, the bromine/methanol etch was used to form a highly doped Te layer as described in the last section prior to contacting with a high work function metal such as gold. An interesting aspect of nearly all back contacts used in CdTe devices is the presence of
copper and a thermal treatment to promote copper diffusion into the CdTe layer. Copper is an essential dopant in high performance cells.

**2.3.5.1 High temperature sputter deposited ZnTe:Cu/Ti**

The Unifilm PVD-300 system described in Section 2.1.3 was used to deposit ZnTe:Cu/Ti bilayers immediately following an Ar ion beam etch described in Section 2.3.4.3. The ZnTe:Cu was deposited by rf magnetron sputtering from a 2 at. % Cu₂Te/ZnTe round target (Materion, Inc.) in pure Ar. The pressure was maintained at 10 mTorr and the power was 26 W over the 3-in target. Copper diffusion was promoted by the substrate temperature of 320 °C. Next, the Ti layer was DC magnetron sputtered from a Sloan ring target in an Ar ambient. The pressure was maintained at 11 mTorr, and the power was ~135 W.

**2.3.5.2 Room temperature evaporated copper/gold**

Bilayer copper/gold films were deposited by evaporation. Film thicknesses were ~5 nm and ~150 nm for the copper and gold layers, respectively. Several unsuccessful attempts were made to photolithographically isolate these cells. Two problems were encountered: (1) gold etchants have a much higher etch rate for CdTe than for gold, and (2) the gold layers were porous to the FeCl₃ etch and/or allowed significant undercutting. To avoid the need for standard photolithography and mesa isolation, the copper and gold layers were deposited through shadow masks containing the desired cell features: a 4 × 4 array of 0.083 cm² circles. The chamber was opened between depositions to replace the source material. Later, a 30-min anneal of the device stack was performed at 260 °C in an inert ambient to drive copper diffusion into the CdTe layer.

**2.3.6 Photolithography, cell isolation, and TCO contacting**

The cells containing ZnTe:Cu/Ti back contacts were isolated using photolithography and two liquid etches. Shipley’s 1818 photoresist was spin coated onto the back contact surface.
After a 5-min soft bake at 100 °C, the substrate was exposed to 190 nm UV light for 35 s through a mask containing the desired cell shapes. Most commonly, a $4 \times 4$ array of $5 \text{ mm} \times 5 \text{ mm}$ square features was used. Substrates were placed in Microposit MF-319 developer solution (Dow Chemical) for ~2 min to remove exposed photoresist. The photoresist was hardened using a 10-min hard bake at 100 °C. The titanium was removed using TFT etch solution (Transene Company, Inc.) for ~20 s. In the final isolation step, the ZnTe and CdTe layers were etched using a 39% solution of FeCl$_3$ in water. The FeCl$_3$ etch was reused until its potency diminished ~50%, so the required etch times were 4–10 min. Indium was soldered around the perimeter of outer cells to provide a low resistance contact for measurement. Figure 2-15 displays the final appearance of these substrates.

![Diagram](https://via.placeholder.com/150)

**Figure 2-15:** Plan view of completed devices after cell isolation and indium solder placement.

Slight modifications were made for the cells with copper/gold contacts. In this case, the photolithography mask contained a $4 \times 4$ array of $0.11 \text{ cm}^2$ circles that were concentric with the deposited gold circles. Only the FeCl$_3$ etch was used in this case. Because the photolithography mask features are larger than the deposited gold circles, a thin ring of unetched CdTe remained in the final cells. Dr. William Rance, a post-doctoral fellow at NREL, determined that outside
area collection contributes 4–8% additional current to the cell. Figure 2-16 displays the final appearance of these substrates.

![Plan view of completed devices using a copper/gold back contact after cell isolation and indium solder placement.](image)

**Figure 2-16**: Plan view of completed devices using a copper/gold back contact after cell isolation and indium solder placement.

### 2.4 Solar Cell Characterization Methods

Completed solar cells were analyzed as a means of optimizing layer properties. Current-voltage measurement was used to obtain cell efficiency ($\eta$), open-circuit voltage ($V_{OC}$), short-circuit current density ($J_{SC}$), and fill factor (FF), while quantum efficiency provided collection information relevant to front contact processing.

#### 2.4.1 Current-voltage measurement

A novel system built by Dr. Matthew Reese at NREL was used. Four probes were electrically contacted to the front and back contacts of the cell. Two of the probes were connected to a voltage source, while the other two measured current. Voltage sweeps were performed both in the dark and during illumination with a lamp referenced to 100 mW/cm$^2$. Figure 2-17 displays an example J-V curve. The $J_{SC}$ and $V_{OC}$ points are highlighted, which occur at the y- and x-intercepts of the J-V curve, respectively. The fill factor is the product of
maximum power ($J_{MP} \times V_{MP}$) divided by $J_{SC} \times V_{OC}$, or the area of the brown box divided by the area of the combined brown and green boxes. Solar cell efficiency $\eta$ is calculated by:

$$\eta = \frac{P_{output}}{P_{input}} = \frac{J_{SC} V_{OC} FF}{100 \text{ mW/cm}^2} \tag{2-28}$$

**Figure 2-17:** Example J-V curve exhibiting $J_{SC}$, $J_{MP}$, $V_{OC}$, $V_{MP}$, the maximum power point, and the rectangles used for calculation of the fill factor.

### 2.4.2 External quantum efficiency

Quantum efficiency is a measure of the ability of the cell to produce electron-hole pairs and collect these carriers. The wavelength-dependent external quantum efficiency (EQE) used in this work is defined as the number of collected carriers divided by the number of incident photons. This definition lumps all parasitic losses together, such as light reflection and absorption in the glass, TCO, and CdS layers, incomplete absorption in the CdTe layer, and recombination. The integrated product of the EQE curve and $G_{AM1.5G}$, the AM1.5G solar spectrum, is equal to the current density. At zero bias, the relation is
\[ J_{SC} = \int_{\lambda_1}^{\lambda_2} \text{EQE}(\lambda) \cdot G_{AM1.5G}(\lambda) \, d\lambda \]  \hspace{1cm} (2-29)

Probes are connected to the cell in the same manner described in Section 2.4.1. Current generation in the device is measured at discrete wavelengths in the spectral range of interest. Figure 2-18 displays the ideal EQE for a CdTe device along with a measured one obtained in this work. The ideal EQE is 100% in the approximate range 300–860 nm, assuming a stoichiometric CdTe absorber. In this case, the real EQE extends to higher wavelength than the ideal EQE based on instrument wavelength uncertainty and/or modified CdTe band gap due to sulfur diffusion. Two of the primary losses in real cells are reflection and absorption by the Glass, TCO, and CdS layers. Losses in the TCO and CdS layers are related to material quality. In Chapter 3, the optical properties of CTO films are analyzed with respect to multiple processing conditions and electrical properties. In Chapter 4, the short wavelength EQE of completed devices will be correlated to as-deposited CdS properties. In Chapter 5, novel techniques are developed to enable characterization of the window layer in completed devices.
Figure 2-18: Plots of ideal and example CdTe EQE.
CHAPTER 3
THE INFLUENCE OF CADMIUM SULFIDE AND CONTACT ANNEALING
CONFIGURATION ON THE PROPERTIES OF HIGH-PERFORMANCE CADMIUM STANNATE

This chapter presents investigations undertaken to understand the conventional cadmium stannate process and develop new processes that are compatible with roll-to-roll processing. This work is adapted from its published form in Solar Energy Materials and Solar Cells [79].

3.1 Introduction

Glass coated with an n-type transparent conductive oxide (TCO) serves as the foundation for solar cell technologies that employ the superstrate configuration. Cadmium stannate (CTO, \( \text{Cd}_2\text{SnO}_4 \)) possesses excellent electrical and optical properties, and is therefore a potential alternative to conventional TCOs such as tin-doped indium oxide (ITO) and fluorine-doped tin oxide (FTO) [80]. Its high mobility (\( \sim 60 \text{ cm}^2/\text{V-s} \)) enables extremely low resistivity (\( \sim 2 \times 10^{-4} \Omega\)-cm) while providing high transmission across both the visible and near infrared (NIR) [81].

CTO is an attractive TCO for a range of optoelectronic applications, particularly cadmium telluride (CdTe) solar cells, because it is comprised of earth-abundant elements and displays robust chemical and thermal stability [81-83]. As a case in point, substitution of the conventional fluorine-doped tin oxide (FTO)/tin oxide (TO) bilayer with a CTO/zinc tin oxide bilayer enabled the National Renewable Energy Laboratory (NREL) to produce a then-world-record 16.7%-efficient CdTe solar cell in 2001 [15, 84].

CTO has comparable resistivity and significantly greater mobility and transmission than FTO [25, 85], but large-scale commercialization has been hindered in part by processing
constraints. The standard procedure for producing state-of-the-art films involves a two-step process: (1) room-temperature sputtering in an Ar, O₂, or Ar/O₂ ambient followed by (2) high-temperature annealing in which the CTO film is placed in direct contact with a glass plate coated with CdS [81, 86-90]. The latter step is commonly referred to as the proximity anneal. Although the orthorhombic phase is dominant in CTO sputtering targets, sputtered films are often amorphous or crystallize in the cubic inverse spinel structure [91, 92]. Previous researchers credited the proximity anneal with promoting crystallization and shifting the Cd:Sn composition to the stoichiometric 2:1 ratio [81, 87, 88, 90]. The annealing temperature is also important. Crystallization begins around 550 °C, and previous work reported optimum conductivity at ~650 °C [27, 81, 87, 88, 90]. Decomposition of the spinel structure begins at ~700 °C, leading to the formation of a SnO₂ phase [27, 90]. The role of sputtering ambient is also unsettled, and it is most likely target dependent. Whereas previous work at NREL reported CTO films sputtered in pure O₂ [81, 89], other groups have reported high-quality films using sputtering ambient compositions up to 90%–100% Ar [27, 87, 88].

The proximity anneal is a major limitation for in-line processing of large-area substrates. Manufacturing would require the production of large, uniform auxiliary CdS films. Moreover, these CdS films are depleted during processing, generating additional process complications. It also presents significant challenges for roll-to-roll (R2R) production due to the requirement of physical contact between the CTO and CdS films. Though not completely understood, the proximity anneal likely serves two necessary functions: providing a Cd source to compensate for stoichiometric deviations in the sputtered film and/or a physical barrier to prevent Cd evaporation during film crystallization [93]. The goals of this work are to better understand this
process and develop alternative processing routes that are more compatible with large-scale manufacturing and R2R production.

First, the impact of sputtering ambient and annealing temperature using the standard proximity anneal is examined. Next, the potential of sputtering CTO/CdS bilayers as an alternative to the proximity anneal, and annealing these bilayers with and without a glass cover plate is examined. Detailed evaluation of the films’ structural, optical, and electrical properties is provided to help understand the process-structure-performance relationships in this system.

3.2 Materials and Methods

Depositions were performed in a CVC SC-3000 sputtering system with a target-to-substrate distance of 7 cm (see Section 2.1.1). The CTO films were radio frequency (rf) magnetron sputtered on 1.5 × 1.5 in² pieces of Corning Eagle XG glass at room temperature and a power of 110 W to a nominal thickness of 175 nm. Upon reaching a base pressure of 2×10⁻⁶ Torr, Ar and/or O₂ flow (total 15 sccm) commenced and the plasma was ignited. The ambient composition was determined using Equation (2-2). Gas flow was controlled by calibrated mass flow controllers, and the chamber pressure was set to 15 mTorr by a hand-operated gate valve. The sputtering target was a 2-in diameter hot-pressed target (Cerac Inc.) consisting of a pre-reacted 2:1 CdO:SnO₂ molar ratio, as described by Haacke and coworkers [90]. CdS films were sputtered in the same chamber at room temperature at 15 mTorr and 15 sccm Ar flowing ambient. The CdS target was a 2-in diameter hot-pressed target (99.99% purity, Cerac Inc.). Whereas CdS films used in the proximity anneal were deposited on larger 3 × 3 in² plates at 70 W with a target-to-substrate distance of 9 cm, these values were 50 W and 7 cm, respectively, for CdS films in CTO/CdS bilayers. After sputtering, the 3 × 3 in² plates were cut into four 1.5 ×
1.5 in\(^2\) plates to supply CdS films for the proximity anneal. Each anneal removes ~10 nm from the CdS film.

High-temperature annealing was performed in a close-spaced sublimation chamber for 15 min in a 30 Torr He ambient. Figure 3-1 displays schematic diagrams of the geometric configurations used for the (a) proximity, (b) covered, and (c) uncovered annealing procedures. The proximity anneal was performed by placing the CTO and CdS films in contact between two temperature-monitored graphite susceptors. Four heating lamps supplied heat to the assembly. Covered annealing of CTO and CTO/CdS bilayers was performed by placing a Corning Eagle XG glass plate directly in contact with the film. CTO and CTO/CdS films were also annealed without a glass cover. The uncovered configuration allows for a variable gap between the CTO film or bilayer and the upper graphite susceptor. The thermal stability of the Corning Eagle XG substrate enabled the CTO films to be successfully annealed up to 700 °C because of the glass’s high annealing point (722 °C) [94]. In contrast, films annealed at 700 °C using Corning 7059 (639 °C annealing point) [70] had more than double the resistivity, and this process caused visible damage to the glass itself.

Figure 3-1: Schematic orientation for (a) proximity, (b) covered, and (c) uncovered anneals.

Film thickness, transmittance/reflectance, and optical band gap were measured using spectroscopic ellipsometry (J.A. Woollam Co., Inc. alpha-SE), spectrophotometry (Cary 5000),
and Tauc plot analysis, respectively. Ellipsometry measurements were checked using contact profilometry (Veeco Dektak 8). Electrical properties (resistivity, mobility, and carrier concentration) of a $1 \times 1$ cm$^2$ section of each sample were determined using Hall measurement (Bio-Rad HL5500PC). Film composition and crystallinity were evaluated by energy-dispersive X-ray spectroscopy (EDAX; JEOL JSM-7000F SEM) and X-ray diffraction (XRD; Siemens Kristalloflex 810), respectively.

3.3 Results and Discussion

A set of films was sputtered under varying ambient compositions ranging from pure O$_2$ to pure Ar, and subsequently proximity annealed under identical conditions. Figure 3-2 plots the deposition rate and resistivity of these films as a function of argon content in the sputter ambient. The deposition rate increased monotonically with the Ar fraction. Using a pure Ar ambient, the sputtering rate was more than four times greater than using a pure O$_2$ ambient. Sputtering with at least 20% O$_2$ produced films with resistivities of $\sim 2.2 \times 10^{-4}$ Ω-cm, and the resistivity was not very sensitive to oxygen content in the range of 20%–100%. Films sputtered in pure Ar were an order of magnitude less conductive ($2.8 \times 10^{-3}$ Ω-cm); note the axis break in Figure 3-2. Lack of oxygen in the films may in part have caused the large increase in resistivity while also affecting crystallinity, as shown later in this chapter. Sputtering in Ar/O$_2$ mixtures provides a means of increasing sputtering rate by more than a factor of three without negatively affecting film conductivity. Film electrical and optical properties were not sensitive to proximity-annealing temperature from 600 °C to 700 °C for films sputtered in pure O$_2$. Neither film resistivity ($2.2$–$2.4 \times 10^{-4}$ Ω-cm) nor the optical band gap ($3.1$–$3.2$ eV) varied significantly as a function of annealing temperature. These data, along with Figure 3-2, demonstrate that CTO sputter
deposition followed by the proximity anneal is a robust process over large ranges of sputtering ambient composition and annealing temperature.

![Graph showing sputtering rate and resistivity as a function of ambient composition.]

**Figure 3-2:** Sputtering rate and resistivity as a function of ambient composition.

Figure 3-3 displays XRD patterns for as-deposited and annealed films. Reference patterns for CTO and SnO$_2$ are also provided [92, 95]. The as-deposited films were amorphous, as expected. After annealing, most of the films were polycrystalline with no preferential orientation. Although not shown here, films sputtered in pure Ar remained amorphous even after the proximity anneal, explaining their high resistivity. Presumably these films are somewhat oxygen deficient, which inhibits crystallization [96]. Films annealed at 700 °C showed narrower peak widths, indicating improved crystallinity. However, the emergence of a small peak at 26.5° (see inset) suggests the onset of CTO decomposition and SnO$_2$ formation, as reported previously [27, 90].
Next, annealed CTO/CdS bilayers were examined as an alternative to the proximity-annealing process. CTO films approximately 175 nm thick were sputtered in pure O$_2$. CdS films of varying thickness were subsequently sputtered onto the CTO films in pure Ar, and these bilayers were annealed at 650 °C. Figure 3-4 displays resistivity, mobility, and carrier concentration for the annealed bilayers as a function of CdS thickness. Note that values obtained from the proximity anneal (circles) are included in Figure 3-4 for reference. In this case the gap between the film and susceptor for the uncovered annealing was 1 mm.

For covered samples, the resistivity decreased with CdS thickness to 10 nm, and increased slightly for thicker CdS layers. Notably, this is the approximate CdS thickness that is lost from the auxiliary CdS film during the proximity anneal. The minimum resistivity value (1.9×10$^{-4}$ Ω-cm) achieved using a bilayer was superior to the proximity anneal (2.2×10$^{-4}$ Ω-cm). The improvement in resistivity was primarily due to increased carrier concentration, since the...
mobility monotonically decreased with CdS thickness. The carrier concentration increased with CdS thickness to 10 nm, reaching a maximum of 5.9×10^{20}/cm^3, which was greater than the carrier concentration of the proximity-annealed film (5.0×10^{20}/cm^3). Above 10 nm, the carrier concentration decreased, and as will be shown below, XRD analysis reveals residual CdS on the surface of these films after annealing. The downward trend in mobility may be caused by residual cadmium and/or sulfur.

The electrical properties of the uncovered films were insensitive to CdS thickness over the range investigated. This suggests that the CdS layer may quickly evaporate before it interacts with the underlying CTO. The resistivity of the uncovered films increased 50% to ~3×10^{-4} \text{ } \Omega \text{-cm}, though these films displayed superior electron mobility (~60 \text{ cm}^2/\text{V-s}).

Notably, high-quality films were produced without exposure to CdS. Resistivity, mobility, and carrier concentration for covered and uncovered CTO were 3.0 and 2.9×10^{-4} \text{ } \Omega \text{-cm}, 67 and 60 \text{ cm}^2/\text{V-s}, and 3.1 and 3.6×10^{20}/cm^3, respectively. Although these films were less conductive than the best CTO produced using CdS, their mobility was significantly higher (67 vs. 54 \text{ cm}^2/\text{V-s}). These results suggest that while the high-temperature anneal is required to achieve both high mobility and conductivity, the CdS primarily serves to increase or maintain the carrier concentration. Haacke and coworkers initially made this conclusion [90]. The addition of CdS may be entirely unnecessary—and undesirable—for applications that do not require resistivity lower than 3×10^{-4} \text{ } \Omega \text{-cm} or in applications that require high IR transmission. Previous work on CTO produced without a CdS anneal is consistent with these results. Meng and coworkers [88] reported CTO films annealed uncovered in Ar at 650 °C for 30 min with comparable resistivity (~3.3×10^{-4} \text{ } \Omega \text{-cm}).
Figure 3-4: Electrical properties as a function of CdS film thickness for uncovered and covered annealing regimes; film produced by the proximity anneal shown for comparison. Films were sputtered in O$_2$ and annealed at 650 °C.
Lastly, the sensitivity of the film properties to the gap between the CTO film and upper heating susceptor was examined, as shown in Figure 3-1(c). Figure 3-5 compares the electrical properties of annealed CTO (without CdS) as a function of gap width to the standard proximity anneal. Films annealed in contact with glass or with a very small (1 mm) gap had a resistivity of ~3×10⁻⁴ Ω-cm. The resistivity increased to ~3.8×10⁻⁴ Ω-cm when the gap increased to 6 mm, but further gap increases did not impact resistivity. These results suggest that the presence of both extra Cd and a barrier to evaporation (glass) are important for the proximity anneal. It is plausible that the resistivity increased with increasing gap distance due to cadmium deficiency. The as-deposited CTO is slightly cadmium-deficient, and additional cadmium can be lost through evaporation during the annealing process. The presence of a glass cover plate prevents cadmium loss during annealing, resulting in a lower resistivity. For uncovered films, the gap distance controls the degree of cadmium sublimation. Additional cadmium, supplied either in the form of a CdS bilayer or a CdS source plate, is required to achieve the lowest resistivity films (~2×10⁻⁴ Ω-cm). Mobility decreased monotonically with increasing gap distance, from 67 cm²/V-s at 0 mm (covered) to 45 cm²/V-s at 20 mm. The mobility at 1 mm was very close to that of the proximity-annealed film. The carrier concentration was insensitive to gap distance, yielding values (3–4×10²⁰/cm³) that were lower than the proximity-annealed film.

Figure 3-6 displays XRD patterns of CTO and CTO/CdS structures annealed in the covered configuration along with references for CTO and CdS [92, 97]. Bilayers with less than 30 nm of CdS displayed patterns nominally identical to those of the proximity-annealed films, containing only peaks associated with CTO. Bilayers incorporating 30 nm CdS displayed a peak at 26.5°, indicating the presence of CdS. EDAX measurements confirmed that significant sulfur was present in this bilayer (~10 at. %), whereas only a negligible quantity (<1 at. %) was
Figure 3-5: Electrical properties of annealed CTO films as a function of film susceptor gap compared to the standard proximity anneal.
detected in films treated with the proximity anneal. Figure 3-7 displays XRD patterns obtained from films/bilayers annealed uncovered with a gap of 1 mm. These were very similar to the covered samples in that CTO and CTO/CdS bilayers up to 30 nm CdS displayed only the characteristic CTO peaks. CdS was detected in the uncovered CTO/50 nm CdS film, though its intensity was less than in the covered case.

**Figure 3-6:** XRD patterns of select CTO and CTO/CdS films annealed in the covered configuration. Reference CTO and CdS patterns shown for comparison.

Maintaining high film transmission across a large spectral region is also essential for photovoltaic (PV) applications. Figure 3-8 compares the transmittance of selected films to bare Corning Eagle XG glass. Corning Eagle XG glass is more than 90% transparent throughout the NIR and visible wavelengths. Proximity-annealed films had an optical band gap of about 3.2 eV but exhibited the lowest NIR transmittance due to free carrier absorption. The spectrum for the covered CTO/10 nm CdS film nearly matches that of the proximity-annealed film, further
evidence of their similarity in film quality. The covered CTO/30 nm CdS film exhibited loss in the blue region of the spectrum and an optical band gap (2.45 eV) characteristic of CdS [38], which is consistent with its XRD pattern (Figure 3-6). The uncovered films had lower conductivity, but their optical properties were superior. The spectra for the uncovered film derived from a CTO/30 nm CdS bilayer showed no CdS absorption features, which is consistent with the XRD pattern. Interestingly, this film displayed the highest optical band gap (3.3 eV), although the carrier concentration was lower than all other films (~3×10^{20}/cm^3). All films displayed >70% transmittance out to 1500 nm, though the uncovered films were superior in this regard. Optical performance was consistent with the measurements of mobility and carrier concentration.
Figure 3-8: Transmittance plots for select films; Corning Eagle XG glass shown for comparison.

For quantitative comparison of the relative transmission of each film, $T_{AM1.5}$, the AM1.5G-weighted transmission, was calculated using

$$T_{AM1.5} = \frac{\int_{\lambda_1}^{\lambda_2} G_{AM1.5}(\lambda) T(\lambda) d\lambda}{\int_0^{\lambda_2} G_{AM1.5}(\lambda) d\lambda}$$

(3-1)

where $G_{AM1.5}(\lambda)$ is the AM1.5G irradiance, $T(\lambda)$ is the film transmittance, and $\lambda_1$ and $\lambda_2$ are the minimum and maximum wavelengths [30, 98]. For this calculation the range was bounded by the minimum recorded wavelength of 300 nm and 1,236 nm, which corresponds to a 1 eV band gap absorber. The optical losses from the Corning Eagle XG glass (~8%) were background subtracted, so the $T_{AM1.5}$ values pertain solely to the CTO films. Analogous to Haacke’s figure of merit [18] and previously defined by Barnes and coworkers [99], a weighted figure of merit was calculated using
\[ \Phi_{AM1.5} = \frac{T_{AM1.5}^{10}}{R_s} \]  

where \( R_s \) is the sheet resistance. Electrical quality correlates well with optical quality in these films. Table 1 summarizes \( \Phi_{AM1.5} \) and other opto-electrical properties for films plotted in Figure 3-8. Compared to the proximity-annealed film, the covered CTO/10 nm CdS film had similar weighted transmission and a lower sheet resistance, resulting in the highest figure of merit among the films examined. The covered CTO/30 nm CdS film has poor optical and electrical properties caused by residual CdS, lowering the optical band gap and increasing the resistivity. Again, the uncovered CTO film compares well to the proximity anneal. With a slightly lower AM1.5G-weighted transmission and higher sheet resistance, the figure of merit is 20% lower. The AM1.5G-weighted transmission was largest in the uncovered CTO/30 nm CdS, due to a higher optical band gap and lower carrier concentration. This film transmits 95% of solar photons with energy greater than 1 eV, making it an excellent TCO for PV applications.

CTO films annealed without CdS displayed increased resistivity by 50% compared to the proximity anneal, demonstrating that the addition of CdS is necessary to maximize conductivity. However, films annealed without a cover exhibited the highest mobility. Covered annealing was effective in decreasing the resistivity in CTO/CdS bilayer films, producing nominally identical films to the proximity anneal. Bilayers annealed in the uncovered configuration were very similar to films produced without CdS. Presumably, the CdS layer evaporates before interacting with the underlying CTO film during uncovered annealing.

As a final demonstration of the suitability of the novel deposition/annealing configurations, CdTe devices were fabricated in collaboration with Dr. Hasitha Mahabaduge at NREL using standard proximity annealed CTO and CTO/CdS bilayers that were annealed while covered. The specific CdS capping layer thickness used here, 5 nm, was selected based on
Table 3-1: Opto-electrical properties of CTO films.

<table>
<thead>
<tr>
<th>Property</th>
<th>Proximity Anneal</th>
<th>Covered CTO/10 nm CdS</th>
<th>Covered CTO/30 nm CdS</th>
<th>Uncovered CTO</th>
<th>Uncovered CTO/30 nm CdS</th>
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<tr>
<td>(T_{AM1.5}) (%)</td>
<td>92%</td>
<td>93%</td>
<td>85%</td>
<td>92%</td>
<td>95%</td>
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<tr>
<td>(R_s (\Omega/\text{sq}))</td>
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<td>12.3</td>
<td>18.9</td>
<td>16.3</td>
<td>19.1</td>
</tr>
<tr>
<td>(\Phi_{AM1.5} (10^{-2} \Omega^{-1}))</td>
<td>3.3</td>
<td>4.1</td>
<td>1.1</td>
<td>2.6</td>
<td>3.1</td>
</tr>
<tr>
<td>(E_g (\text{eV}))</td>
<td>3.2</td>
<td>3.2</td>
<td>2.5</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>(\rho (10^{-4} \Omega\cdot\text{cm}))</td>
<td>2.2</td>
<td>1.9</td>
<td>3.1</td>
<td>2.9</td>
<td>3.1</td>
</tr>
<tr>
<td>(\mu (\text{cm}^2/\text{V-s}))</td>
<td>57</td>
<td>54</td>
<td>45</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>(n (10^{20}/\text{cm}^3))</td>
<td>5.0</td>
<td>5.9</td>
<td>4.5</td>
<td>3.7</td>
<td>3.1</td>
</tr>
</tbody>
</table>

previous device results. These devices also incorporated 25 nm zinc tin oxide (ZTO) buffer layers that were proximity annealed, 100 nm CdS:O window layers using the optimized material from Chapter 4, and a 5 nm copper/150 nm gold back contact. Figure 3-9 displays a simple device performance comparison of open-circuit voltage (\(V_{OC}\)), short-circuit current density (\(J_{SC}\)), fill factor (FF), and efficiency. \(V_{OC}\) and FF are slightly better in the device featuring the covered anneal, leading to a modest efficiency improvement of 2% absolute. This is close to the observed deviation in nominally identical substrates. The highest performing device had an efficiency of 15.7%. As stated in Chapter 2, outer area collection in these devices is estimated at 4–8%. These device results are a further indication that the modified schemes introduced in this chapter for producing high-performance CTO front contacts translate to actual devices.

3.4 Conclusions

A variety of sputter-deposition and annealing conditions for CTO were explored. The deposition rate increased significantly as the oxygen content decreased in the ambient, and good electrical and optical properties were maintained at oxygen contents as low as 20%. Alternative sputtering and annealing configurations were developed that are more compatible with large-scale and roll-to-roll manufacturing than the standard proximity anneal. CTO/CdS bilayers annealed with a glass covering were similar in quality to CTO films treated using the proximity anneal. Films annealed without the cover plate had higher transmission and mobility, but
slightly higher resistivity. These data demonstrate that the CTO deposition/annealing process is significantly more robust than previously understood, and that the annealing conditions can be varied to produce films with higher mobility and transparency (uncovered anneal) or higher conductivity (covered anneal). The presence of CdS during the annealing process increases the carrier concentration of the films at a cost of some NIR absorbance losses. The covered annealing configuration introduced in this work was later applied in CdTe devices, with efficiencies at or above those measured using the proximity anneal.

**Figure 3-9:** $V_{oc}$, $J_{sc}$, FF, and efficiency comparison of CdTe devices incorporating CTO layers that were fabricated using the standard proximity anneal and covered annealing of a CTO/5 nm CdS bilayer.
CHAPTER 4
PROPERTIES OF REACTIVELY SPUTTERED OXYGENATED CADMIUM SULFIDE (CdS:O) AND THEIR IMPACT ON CdTe SOLAR CELL PERFORMANCE

This chapter presents investigations on the properties of CdS:O and its use in CdTe solar cells. This chapter is an adaptation of previously published works in the IEEE Photovoltaic Specialists Conference [100] and the Journal of Vacuum Science and Technology A [101].

4.1 Introduction

Cadmium sulfide (CdS) is the most commonly used n-type window layer in thin-film solar cells based on cadmium telluride (CdTe), copper indium gallium diselenide (CIGS), and copper zinc tin sulfide (CZTS) absorbers. Although CdS is a good heterojunction partner to these absorber materials, it is critical to minimize optical absorption in this layer because it does not generate useful photocurrent [25]. The structural, optical, and electronic properties of the CdS layer can greatly impact cell performance. Chemical bath deposition (CBD) is commonly used for CdS deposition and has been used in high-efficiency CdTe cells [25, 102]. However, this solution-based process creates significant amounts of hazardous waste and is difficult to uniformly scale to large-area substrates. CBD-grown CdS has an optical band gap of 2.4 eV [103], and parasitic absorption from this window layer reduces the photon flux to the absorber layer at wavelengths <525 nm by up to 5.8 mA/cm² [104]. The conventional approach to mitigate absorption losses is to reduce the CdS film thickness, which improves current density at the expense of losses in voltage and fill factor [31]. Optimizing this trade-off is further complicated by the potential loss of CdS due to alloying with CdTe [39] and/or chemically
reactive buffer layers [105] that can occur during subsequent high-temperature device processing.

An alternative approach to thinning the CdS layer is to increase its optical band gap through the formation of alloys at either the cation (CdZnS) [106] or anion (CdS:O) site. The latter is typically accomplished by reactive sputtering in a mixed oxygen/argon ambient [38, 107-109]. The sputtering ambient composition is a powerful processing parameter, affecting film crystallinity, optical band gap, and composition. Films sputtered at room temperature in a mixed oxygen/argon ambient exhibit reduced crystallinity and a higher optical band gap than those sputtered in pure Ar [38]. With a higher optical band gap, more photons are transmitted to the absorber and the need for an ultra-thin layer is less important.

The optimal oxygen content in the sputtering ambient for CdTe solar cell performance reported in the literature has varied between 1% and 2.5% O₂/Ar [38, 107, 108, 110]. Process- and target-specific differences are likely to be the primary causes for this fluctuation. Previous studies have focused on identifying the optimal oxygen content for device performance, but there have been limited reports on the resulting film composition or bonding arrangement [111, 112]. As such, the underlying reasons for these variations are not fully understood. The goals of this work are to investigate how the composition of the O₂/Ar ambient affects as-deposited CdS:O film properties, characterize optimal CdTe devices based on CdS:O properties, and identify simple metrics that can be used to optimize device performance. In this study, the effects of varying the O₂/Ar sputtering ambient composition on the intrinsic properties of CdS:O films are quantified and correlated with CdTe solar cell performance. Observed improvements in short-circuit current density (Jₛᶜ) and external quantum efficiency (EQE) are quantitatively consistent
with increases in CdS:O transparency. In working with multiple targets and deposition systems, the optical band gap was determined to be a useful metric for process transfer and scale-up.

4.2 Materials and Methods

CdS:O films were radio-frequency (rf) magnetron sputtered in a CVC SC-3000 diffusion-pumped system (see Section 2.1.1) with a base pressure of $2 \times 10^{-6}$ Torr. A 2-in-diameter, hot-pressed target of 99.99% purity (Materion Corporation) was sputtered in an Ar/O$_2$ ambient with individual gas flow rates set using calibrated mass-flow controllers. The total flow rate was fixed at 15 sccm and the chamber pressure was set to 15 mTorr. The ambient composition in % O$_2$ is calculated using (2-2). Substrates (1.5×1.5 in$^2$) were positioned 7 cm above the target and were not intentionally heated during deposition. The rf power was set at 50 W for all depositions, and the as-deposited CdS:O film thickness in all devices was fixed at 100 nm.

As-deposited films were characterized in terms of thickness, crystallinity, optical transmittance/reflectance, composition, and binding states. Thickness was measured at a step edge between the film and substrate using a stylus profilometer (Veeco Dektak 8). These measurements were used to calibrate a quartz-crystal monitor in the deposition chamber for subsequent depositions. Crystallinity was analyzed by X-ray diffraction (XRD) employing Cu K$_\alpha$ radiation (Rigaku Ultima). Transmittance and reflectance were determined by UV-Vis-NIR spectrophotometry (Cary 5000). The optical band gap was graphically analyzed using direct band gap Tauc plot analysis of the transmittance and reflectance data [58]. Bulk elemental composition was determined using Rutherford backscattering spectrometry (RBS). The RBS instrument was custom-built by NEC and uses He$^+$ ions with 2 MeV incident energy. Films for RBS analysis were deposited on silicon wafers to avoid interference from oxygen and other elements present in glass. Immediately prior to deposition, the wafers were etched in dilute
hydrofluoric acid to remove the native oxide. RUMP software (Genplot) [113] was used to quantify peak areas and determine film composition. Bonding states were determined by X-ray photoelectron spectroscopy (XPS; Physical Electronics 5600). Radiation was provided by a monochromatic Al source, and pass energies of 187.85 and 11.75 eV were used for survey and high-resolutions scans, respectively. The spectra were aligned on the basis of placing the adventitious carbon 1s peak at 284.8 eV and fit with a Shirley background and Voigt line shapes using CasaXPS commercial software (Casa Software Ltd.). In the analysis of the sulfur 2p line, spectra were de-convoluted into three constituents assigned to sulfide (S$^{2-}$), sulfate (SO$_4^{2-}$), and SO$_2$/SO$_3^{2-}$ complexes. The fitting procedure was constrained by fixing the 2p$_{3/2}$:2p$_{1/2}$ area ratio to 2:1 and the spin-orbit splitting to 1.18 eV [65].

CdTe solar cells were fabricated using the superstrate architecture. Fluorine-doped tin oxide, intrinsic tin oxide, CdS:O, CdTe, and a copper/gold back-contact were deposited sequentially on Corning 7059 glass. The tin oxide bilayer was deposited by metal-organic chemical vapor deposition at 550°C and had a sheet resistance of ~20 Ω/sq [114]. The window layer was sputtered in 0%–10% O$_2$/Ar to a thickness of 100 nm. The ~4-µm CdTe absorber was deposited by close-spaced sublimation, in which the source and substrate temperatures were 660° and 600°C, respectively [115]. A vapor-phase CdCl$_2$ anneal was performed at 400°C for 10 min. The CdTe surface was then etched in 0.05 vol. % Br/MeOH for 20 s. Sequential 5-nm copper and 150-nm gold films were then deposited by evaporation at room temperature through a shadow mask with sixteen 0.08-cm$^2$ circular holes. The devices were annealed in a tube furnace at 260°C for 30 min to activate the back contact [116]. The cells were photolithographically isolated using 0.11-cm$^2$ circular features, leaving a small perimeter of unetched CdTe around each cell. Here, $J_{SC}$ and efficiency values are reported on an un-apertured basis. From
comparisons of apertured and non-apertured current density–voltage (J-V) measurements, the estimated current collection from outside the defined area is 4%–8%.

4.3 Results and Discussion

The following subsections present properties of the as-deposited CdS:O films, CdTe device performance when incorporating CdS:O window layers, and efforts to scale up the CdS:O process to two higher productivity tools.

4.3.1 Intrinsic properties of CdS:O films

First, film crystallinity is examined using XRD. Figure 4-1 displays the patterns for films sputtered in various O₂/Ar ambients. Films sputtered in <2% O₂/Ar are polycrystalline with a peak at 2θ = 26.5° corresponding to the (111) cubic and/or the (002) hexagonal orientation, whereas the remaining films sputtered at higher oxygen concentrations are amorphous [100]. Oxygen suppresses crystallinity as reported previously in the literature [38, 107]. For use in CdTe solar cells, amorphous window layers may be preferred due to the large CdS/CdTe lattice mismatch [40].

Next, the optical response of films fabricated under varying oxygen partial pressures was examined. Figure 4-2 displays the transmittance (a) and optical band gap (b) of CdS:O films grown with 0–10% O₂/Ar in the ambient. In the range 500–900 nm, the films have an average transmittance of ~70%. The transmittance falls at lower wavelengths where absorption dominates. Films sputtered in pure Ar have an optical band gap near the expected value of 2.4 eV. The optical band gap increases linearly with oxygen partial pressure in the sputtering ambient up to 2.8 eV at 6% O₂. Above 6%, the shape of the curve becomes steeper and parabolic, with the optical band gap reaching 3.8 eV at 10% O₂. At high oxygen partial pressure, the optical band gap exceeds that of degenerately doped CdO (≤3.1 eV) [118]. This enlarged
Figure 4-1: X-ray diffraction patterns for CdS films grown in sputtering ambients ranging from pure Ar to 10% O₂/Ar. Cubic and hexagonal CdS reference patterns from [97] and [117], respectively.

The optical band gap has previously been attributed to nanoscale effects [112], but could also be caused by formation of other oxidized species.

Bulk compositional analysis of the as-deposited films was performed by RBS, a well-established technique for CdS [119, 120]. This is the first published use of RBS for compositional analysis of sputtered CdS:O films. In contrast to surface-sensitive techniques such as XPS, RBS is able to sample the entire 100-nm film depth and is therefore less susceptible to errors caused by surface contamination. Figure 4-3(a) displays a representative RBS spectrum obtained from a 6% O₂ CdS:O film. The cadmium, sulfur, and oxygen peaks are well separated from each other, allowing robust compositional analysis over a wide range of relative element ratios. The contribution of the underlying silicon was background subtracted, and atomic...
Figure 4-2: (a) Transmittance, and (b) optical band gap of ~250 nm CdS:O films. Intrinsic CdS and degenerate CdO [118] optical band gaps are provided for comparison.

fractions were calculated by dividing peak areas by the square of the atomic number. Figure 4-3(b) displays the atomic % oxygen and cadmium/sulfur ratio for films sputtered in 0%–9% O₂.
The spectrum for the film sputtered in pure Ar does not contain a detectable peak for oxygen. The oxygen content in the films scales linearly with the partial pressure of O\textsubscript{2} in the sputtering ambient up to 6\% O\textsubscript{2}, where the oxygen content is \(~40\) at. \%. Further increasing the sputter ambient oxygen partial pressure results in the film composition saturating at \(~45\) at. \% oxygen. Despite the substantial changes in oxygen content, the cadmium/sulfur atomic ratio remains essentially constant at \(~1.15\) over the range examined. The cadmium/sulfur ratio may be an indicator of relative carrier density, because sulfur vacancies are the primary \textit{n}-type defects [121]. The observed sulfur deficiency may be due to its relatively high volatility and/or preferential sputtering of sulfur from the substrate surface by high-energy plasma ions [122].

To better understand how oxygen is incorporated into the films without altering the cadmium/sulfur ratio, the bonding environment was examined using XPS. Note that these films were exposed to ambient and not sputter cleaned in the XPS instrument, as sputter cleaning often distorts the composition through preferential sulfur removal and subsequent surface rearrangement [123]. Figure 4-4 displays high-resolution spectra from the sulfur 2p region for films deposited with 0, 2, 6, 8, and 9\% O\textsubscript{2}. These spectra were de-convoluted into three components attributed to sulfide (S\textsuperscript{2−}) species, SO\textsubscript{2} or SO\textsubscript{3}\textsuperscript{2−} groups, and sulfate (SO\textsubscript{4}\textsuperscript{2−}) moieties, whose 2p\textsubscript{3/2} peak positions are located at binding energies of 161.7, 166.8, and 168.7eV, respectively [65]. The relative distribution of sulfur bound in the sulfide and oxygenated sulfur (SO\textsubscript{x}) states was evaluated by fitting Voigt line shapes to the respective peaks, as described in Section 4.2. At 0\% and 2\% O\textsubscript{2}, sulfur is present primarily in the sulfide state. The contribution from SO\textsubscript{x} groups is >40\% for films sputtered at >6\% O\textsubscript{2}. 
Figure 4-3: (a) RBS spectrum from a 6% O\textsubscript{2}/Ar CdS:O film illustrating the contributions from cadmium, sulfur, oxygen, and the silicon substrate. (b) Oxygen content and cadmium/sulfur ratio of CdS:O films as determined by RBS.
Figure 4-4: Sulfur 2p X-ray photoemission spectrum of selected CdS:O films. Solid lines represent raw XPS spectra. Dashed lines display the fit obtained by de-convoluting the spectra into contributions of sulfide (S$^{2-}$), sulfate (SO$_4^{2-}$), and SO$_2$/SO$_3^{2-}$ complexes whose 2p$_{3/2}$ peak positions are identified by the vertical lines.

Figure 4-5 displays the atomic distribution of sulfur among its sulfide, sulfate, and SO$_2$/SO$_3$ constituents as a function of sputtering ambient composition. For all films investigated, sulfide is the largest component present. Oxygenated sulfur groups are detected in low concentrations even for the film sputtered in pure Ar. Since oxygen was not detected in this film by RBS, the presence of these species is attributed to surface contamination. Sulfate and SO$_2$/SO$_3$ concentrations increase systematically with increasing O$_2$ in the sputtering ambient to ~34% and ~18% at 9% O$_2$, respectively. Throughout the range examined, oxygen is observed to preferentially incorporate in sulfate groups rather than as SO$_2$/SO$_3$ complexes.
The relative distribution of sulfur, as well as the oxygen/sulfur and cadmium/sulfur ratios measured by RBS and XPS, are tabulated in Table 4-1. The SO\textsubscript{x} fraction of films grown with 0% O\textsubscript{2} is ~15%, which is attributed to surface contamination because oxygen was not detected by RBS. The contribution from oxygenated sulfur species increases with the sputtering ambient oxygen partial pressure; at >6% O\textsubscript{2}, sulfur is present predominantly in the form of SO\textsubscript{x} groups. The cadmium content was evaluated as described in Section 4.2 using Cd 3d line scans. The Cd 3d spectra were fit by constraining the 3d\textsubscript{5/2}:3d\textsubscript{3/2} area ratio and spin-orbit splitting to 3:2 and 6.74 eV, respectively. The relative elemental abundances were calculated based on the quotients of the total elemental areas and the relative sensitivity factors of each element. XPS measurement of the cadmium/sulfur ratio indicates that the films are slightly cadmium-rich and unchanging with the sputtering ambient composition, in excellent quantitative agreement with RBS. Quantitative evaluation of the oxygen/sulfur ratio based on the O 1s signal was...
problematic due to uncertainties associated with surface contamination. The unchanged cadmium/sulfur ratio observed by both RBS and XPS suggests that oxygen incorporates primarily through the replacement of $S^{2-}$ with $SO_x$ groups. To test this hypothesis, the oxygen content was evaluated based on the sulfur 2p line scan assuming that oxygen was incorporated exclusively in the form of $SO_x$ groups. In this calculation, the $SO_2/SO_3^{2-}$ groups were assumed to have a 2.5 oxygen/sulfur ratio. With the exception of the 0% $O_2$ sample, there is very good agreement between this calculation and the oxygen/sulfur ratio evaluated by RBS, agreeing with the hypothesis that oxygen is incorporated primarily in the form of $SO_x$ groups as opposed to mixtures of CdS and CdO.

Table 4-1: CdS:O film composition determined by XPS and RBS

<table>
<thead>
<tr>
<th>Ambient</th>
<th>XPS SOx/(S + SOx)</th>
<th>XPS Cd/S</th>
<th>RBS Cd/S</th>
<th>XPS O/S$^\dagger$</th>
<th>RBS O/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% $O_2$</td>
<td>0.15*</td>
<td>1.14</td>
<td>1.11</td>
<td>0.54*</td>
<td>0.00</td>
</tr>
<tr>
<td>2% $O_2$</td>
<td>0.21</td>
<td>1.11</td>
<td>1.09</td>
<td>0.74</td>
<td>0.49</td>
</tr>
<tr>
<td>6% $O_2$</td>
<td>0.41</td>
<td>1.14</td>
<td>1.15</td>
<td>1.41</td>
<td>1.48</td>
</tr>
<tr>
<td>8% $O_2$</td>
<td>0.55</td>
<td>1.13</td>
<td>1.18</td>
<td>1.98</td>
<td>1.90</td>
</tr>
<tr>
<td>9% $O_2$</td>
<td>0.52</td>
<td>1.16</td>
<td>1.18</td>
<td>1.83</td>
<td>1.77</td>
</tr>
</tbody>
</table>

* Attributed to surface contamination
† Calculated from sulfur 2p results assuming that oxygen is only present in the films as $SO_x$ groups

CdS sputtered in pure Ar has many similar characteristics to CBD-deposited material: polycrystalline, low oxygen incorporation [124], and an optical band gap of ~2.4 eV. The addition of oxygen to the sputtering ambient reduces crystallinity, greatly increases oxygen incorporation by forming oxygenated sulfur complexes, and increases the optical band gap. In the next section, CdTe solar cell results are presented and correlations between device performance and CdS:O film properties are discussed.
4.3.2 Device performance

CdTe solar cells fabricated with 100-nm CdS:O window layers were characterized using J-V and EQE measurements. The only manipulated variable was the CdS:O sputtering ambient composition. Figure 4-6(a) displays the EQE spectra as a function of the sputtering ambient composition. The blue EQE (300–600 nm) increases monotonically with O$_2$ partial pressure in the sputtering ambient. The red EQE response (>600 nm) remains unchanged up to 6% O$_2$, but then declines slowly at 7% (not shown) and 8% O$_2$ before completely collapsing in devices fabricated with 9% O$_2$. A common characteristic of recent champion CdTe cells is their high EQE at short wavelengths, with values at 400 nm ranging from ~70–90% [25, 125]. The EQE at 400 nm in our optimal device using 6% O$_2$ falls well short of these record values (57.2%), suggesting that additional considerations are required for state of the art performance. Options for improving blue EQE include replacing FTO with a more transparent TCO such as cadmium stannate [79], reducing the CdS:O layer thickness, and using a different buffer material. Figure 4-6(b) displays the current-voltage response for the same set of cells. Cells with CdS:O grown in the 0%–8% O$_2$ range have good rectifying behavior but exhibit rollover associated with Schottky barrier formation at the back contact [126]. Rollover in these cells is most likely a result of excess copper and/or sub-optimal diffusion of copper during the back contact annealing step. Note that similar cells fabricated with ZnTe:Cu/Ti back contacts did not exhibit rollover. Maximum J$_{SC}$, open-circuit voltage (V$_{OC}$), fill factor (FF), and efficiency are achieved with the 6% O$_2$ CdS:O layer. Going from 0% to 6% O$_2$, the J$_{SC}$ increases from 22.4 to 25.6 mA/cm$^2$, in quantitative agreement with calculated J$_{SC}$ values extracted from the EQE data. In addition, improvements are also observed in V$_{OC}$ (806 to 830 mV) and FF (60.4% to 68.0%). Overall
efficiency improves from 10.8% to 14.5%. At 9% O$_2$, the devices no longer show rectifying behavior, which is consistent with the collapse in the EQE.

**Figure 4-6:** (a) EQE; and (b) J-V curves of CdTe cells fabricated with 100-nm CdS:O window layers. The different percentages indicate the relative abundance of oxygen in the O$_2$/Ar sputtering ambient.
The improvements in $J_{SC}$ are well correlated with the increased transparency of the as-deposited CdS:O films. Figure 4-7 compares the Ultraviolet–visible–near-infrared (UV-Vis-NIR) transmission spectra of as-deposited CdS:O films with the EQE of the resulting CdTe devices. Remarkably good agreement is observed between the CdS:O absorption edge position and the EQE response of the completed cells over the full range examined. The relative fit between short-wavelength film transmittance and device EQE is best in the 9% $O_2$ case, is slightly worse for 6% $O_2$, and is worst for 0% $O_2$. For 0% and 6% $O_2$, the measured EQE is in fact greater than the film transmittance in the as-deposited CdS:O layer. One plausible explanation is that CdS:O/CdTe interdiffusion leads to reduced attenuation in the 300–500 nm region through consumption of a portion of the CdS:O layer. The goodness of fit between the film transmittance and device EQE is somewhat surprising because thermal annealing studies in inert environments at device processing temperatures (~600ºC) by ourselves and others [107, 127] show that the CdS:O decomposes to material with an optical band gap equivalent to that of intrinsic CdS, presumably of reduced thickness. A simple reduction in CdS thickness would improve transmission but would not significantly shift the position of the absorption edge. One plausible explanation for the abrupt and catastrophic failure observed at 9% $O_2$ is provided in Section 4.3.3.

4.3.3 Impact on CdS:O/CdTe heterojunction alignment

Here, an attempt is made to explain the abrupt loss of rectifying behavior and quantum efficiency observed at 9% $O_2$ (Figure 4-6). One plausible cause for this catastrophic failure is the presence of a significant conduction band offset at the CdS/CdTe junction [128]. Similar behavior has been observed both experimentally [129] and in modeling studies [130] of CIGS heterojunctions. To better understand these changes idealized band diagrams of the CdTe/CdS:O
heterojunction were constructed based on the measured valence band maximum (VBM) energy position offset from the Fermi level using XPS. Figure 4-8 displays the low energy XPS spectra obtained from CdS:O films deposited with 0, 2, 6, 8, and 9% O\textsubscript{2} in the sputter ambient. The position of the valence band maximum relative to the Fermi level, $E_F - E_{VBM}$, is determined by the x-intercept of a fit of the linear portion of the spectrum [131]. The error of this measurement is estimated to be ±0.1 eV based on the scan resolution. With no oxygen present the offset from the Fermi level was 1.8 eV, similar to previous measurements of intrinsic CdS [132]. This offset increased slightly to 2.0 eV at high O\textsubscript{2} levels. Recall that the optical band gap increased ~1 eV over this range (Figure 4-1), suggesting that the conduction band minimum (CBM) energy must shift upward significantly to accommodate the majority of the band gap increase.


Based on data from Figures 4-2(b) and 4-8 idealized band diagrams were constructed for the CdS:O/CdTe heterojunction. Figure 8 displays ideal band diagrams for three CdS sputtering ambient compositions using the band diagram for CdTe published in [132]. The position of the VBM and CBM in bulk CdS:O relative to the Fermi level were determined experimentally by XPS and the optical band gap, respectively. To estimate the degree of band bending at the interface, the CdS work function was assumed to remain unchanged (4.8 eV) [132]. The conduction band offset (CBO) at the CdS/CdTe interface was calculated using the electron affinity rule:

$$\text{CBO} = e\chi_{\text{CdTe}} - e\phi_{\text{CdS:O}} + E_{g,\text{CdS:O}} - \left(E_{F,\text{CdS:O}} - E_{\text{VBM,CdS:O}}\right)$$  \hspace{1cm} (4-1)$$

where $\chi$ is the electron affinity and $\phi$ is the work function. In Figure 4-9(a), the band diagram for 0% CdS:O exhibits a small spike at the CdS/CdTe interface caused by a positive CBO.

**Figure 4-8:** High-resolution valence band maximum (VBM) energy X-ray photoemission spectrum. Sloped dashed lines represent linearized portions of the spectra for VBM energy determination. Extracted VBM energies are indicated by vertical dashed lines.
Reference [133] gives a similar value for an evaporated CdS/CdTe interface. Figure 4-9(b) displays the band diagram at the optimal condition for cell performance (6%). At this condition a moderate, positive CBO of 0.4 eV is expected which has been shown to be near-ideal in CIGS heterojunctions. Finally at 9% O\textsubscript{2} (Figure 4-9c) the CdTe/CdS:O heterojunction has a significant CBO of +0.8 eV which presents a significant barrier to electron collection. Modeling studies [130, 134] predict and experiments [129] have demonstrated a precipitous drop in J\textsubscript{SC} when the CBO exceeds 0.5 eV, which is in excellent agreement with these experimental results.

\textbf{Figure 4-9:} Idealized band diagrams for (a) 0% O\textsubscript{2} CdS:O/CdTe, (b) 6% O\textsubscript{2} CdS:O/CdTe, and (c) 9% O\textsubscript{2} CdS:O/CdTe. The work function for CdS (4.8 eV) and the band diagram for CdTe are from [132].
4.3.4 Process transfer

The optimum sputtering ambient composition observed in this work (6% O$_2$) is significantly different than in previous reports. It is also notable that the optimal value of 2% O$_2$ reported by Wu and co-workers was achieved using the same sputter deposition system, albeit with a different CdS target [38]. The ambient composition reported in this work is based on the set points of the electronic mass flow controllers (MFC) employed. To confirm their accuracy the two MFCs were independently calibrated by measuring the partial pressure generated at the set points employed using an ion gauge with the gate valve fully open. Figure 4-10 displays the pressure measured when flowing the two gases individually (circles). In each case a linear dependence was observed over the range employed, and the resulting O$_2$/Ar percentage based on these measurements (black squares) very closely matched the nominal set point (black line).

![Figure 4-10: Sputter chamber pressure for O$_2$ and Ar (circles); measured percentage of O$_2$ to Ar (squares); set point percentage of O$_2$ to Ar (line). The total flow rate for each set point is 15 sccm.](image-url)
Moreover, after exhausting the target that was used to generate the data shown in this chapter, a second CdS target was obtained from the same manufacturer with nominally identical material specifications as the original target. Similar device performance (>14%) was achieved, but the ambient composition required for optimal performance shifted to 4% O₂, further illustrating the sensitivity of this process to target material quality, fabrication, composition, and reproducibility. Subsequently, the CdS:O process was scaled up to two systems that employ a 3-in CdS target, enabling the use of larger 3×3 in² substrates. The Kurt J. Lesker (KJL) CMS 18 (see Section 2.1.2) is a turbo-pumped system with a base pressure of ~1×10⁻⁷ Torr that is equipped with a load lock for sample introduction. Depositions in the KJL were performed at 5 mTorr with a sputtering power of 100 W. Using this new system and target, optimal device performance (>14%) was achieved using 4% O₂ in the sputtering ambient. The Unifilm PVD-300 (see Section 2.1.3) is a cryogenic-pumped system with a base pressure of ~1×10⁻⁷ Torr and also contains a load lock. Depositions in the Unifilm were performed at 15 mTorr with a sputtering power of 100 W. Figure 4-11 compares the optimal device efficiency obtained using four system/target combinations. These boxplots compare the efficiency of devices fabricated using 6% O₂ in the CVC with the original target (CVC-old trgt), at 4% O₂ in the CVC with the new target (CVC-new trgt), at 4% O₂ in the KJL with a larger 3-in target (KJL), and at 4% O₂ using the Unifilm and the 3-in target (Unifilm). The tighter distribution in the larger KJL and Unifilm systems is attributed to improved CdS film uniformity. For all four target/system combinations, optimal device performance was attained using sputtering conditions that yield as-deposited CdS:O with a nominally identical optical band gap of ~2.8 eV. Note that this optimum is slightly higher than the value reported by Wu and coworkers, 2.65 eV, although results for cells incorporating CdS:O with other band gaps were not reported [38]. The optimal optical
band gap most likely depends highly on the specific cell architecture and processing employed. However, once established, the CdS:O optical band gap is a simply obtained metric that can be used as a diagnostic tool for optimizing cell performance, both initially and after a target/process/system transfer.

Figure 4-11: Box-plot comparison of device efficiency obtained at optimal conditions with four different chamber/target combinations. Optimal performance was obtained using 6% O$_2$ CdS:O deposited in the CVC chamber using the original target, 4% O$_2$ CdS:O in the CVC using a new target, 4% O$_2$ CdS:O deposited in the KJL chamber using a third target, and 4% O$_2$ CdS:O deposited in the Unifilm system using the third target. In each case, the optical band gap of the as-deposited CdS:O was ~2.8 eV.

4.4 Conclusions

We have correlated the optical, chemical, and electronic properties of sputter-deposited CdS:O films with the performance of resulting CdS:O/CdTe solar cells. Sputter deposition of thin films is more amenable to scale-up than CBD, and reproducible control of the O$_2$/Ar
ambient composition provides an efficient means to tune the intrinsic properties of the window layer. RBS data reveal that optimal films contain 40 at. % oxygen, and XPS data confirm these results and indicate that oxygen incorporation occurs primarily through the formation SOx complexes. The performance of devices incorporating optimized CdS:O benefits from a significant increase in $J_{SC}$ as well as modest improvements in $V_{OC}$ and FF. Comparisons among various sputter-deposition chamber and target combinations reveal that maximum cell efficiency is achieved for our device architecture when the CdS:O optical band gap is ~2.8 eV. The optical band gap is identified as a useful metric to “dial in” the CdS:O sputtering process prior to cell fabrication and quickly re-establish a baseline upon making target/process/system changes.
CHAPTER 5
CHEMICAL AND MECHANICAL TECHNIQUES ENABLING DIRECT
CHARACTERIZATION OF THE CdS/CdTe HETEROJUNCTION REGION IN
COMPLETED DEVICES

This chapter is an adaption and expansion of a paper submitted to the 2015 IEEE Photovoltaic Specialists Conference proceedings [135].

5.1 Introduction

Cadmium sulfide (CdS) is the most commonly used window layer in cadmium telluride (CdTe) photovoltaic devices [136]. This layer presents a receptive surface for CdTe nucleation and growth, and forms a high quality heterojunction with the absorber. Intrinsic CdS is not photoactive, and parasitic absorption in this layer attenuates quantum efficiency (QE) at wavelengths below 520 nm [137]. This issue can be mitigated in part by reducing thickness, but only to a degree as efficiency declines due to deterioration in both open circuit voltage ($V_{oc}$) and fill factor (FF) when the thickness is reduced below 85 nm [138, 139]. The window layer can be deposited by several techniques, including chemical bath deposition (CBD) [140], close-spaced sublimation (CSS) [141], evaporation [142], and sputtering [33]. These processes are typically conducted at low temperature (20–200 °C). Sputtering offers numerous advantages over alternative deposition methods. It is vacuum-based and scalable for in-line manufacturing. Uniformity and waste management issues are inherently 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 in the sputter ambient as first introduced by Wu and coworkers more than a decade ago [38].
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 [143, 144]. 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

$$E_g(y) = 2.40(1 - y) + 1.51(y) - b(1 - y)(y)^{(5-1)}$$

where $y$ refers to the atomic concentration in CdS$_{1-y}$Te$_y$ and $b$ is a bowing parameter equal to $\sim 1.8$ [45]. This alloying process further reduces the band gap of the window layer, and as such it is generally believed that excessive interdiffusion degrades device performance by either reducing the short circuit current density ($J_{sc}$) and/or by shunting caused by localized consumption [29, 142].

The presence of oxygen in CdS has been found to have a dramatic impact on the interdiffusion process. McCandless and Birkmire [145] showed that annealing CdS in a CdCl$_2$O$_2$:Ar environment prior to CdTe deposition eliminated the formation of CdS$_{1-y}$Te$_y$ on the S-rich side of the junction, attributing this behavior to the formation of oxide at grain boundaries. Oxygen is also present in CBD films at levels of 5-15 at. %, and its presence is credited with retarding interdiffusion in a similar manner as O$_2$ annealing [29]. The higher level of oxygen in CBD CdS has been credited with delivering generally higher efficiency than devices fabricated using CdS deposited by CSS or evaporation. The use of reactively sputtered oxygenated cadmium sulfide (CdS:O) was introduced in 2002 by Wu and co-workers [38], who prepared window layers by reactive sputtering a CdS target in an O$_2$/Ar ambient. Based on transmission electron microscopy (TEM) images these authors also attributed the observed improvements in $J_{sc}$ to the ability of CdS:O to suppress Te interdiffusion and alloy formation [146].
For the past decade CBD has remained the predominant technique used to prepare CdS, though in recent years several groups have turned to sputtered CdS:O in order to produce high efficiency devices [108, 127, 128, 147, 148]. These groups have shown that as oxygen is introduced into the sputter ambient, film crystallinity is reduced and the optical band gap increases. Performance gradually improves with increasing optical band gap, reaches a maximum, and thereafter drops dramatically [108, 128, 148]. The oxygen content in the as-deposited films can reach 40 at. %, and it is incorporated primarily as sulfate groups (SO\textsubscript{x}) [128, 148, 149]. The efficiency gains are achieved primarily through increases in $J_{sc}$ due to improvements in short-wavelength quantum efficiency without compromising $V_{oc}$ or FF. Interestingly, all studies [38, 108, 128, 146-148] in which CdS:O was shown to yield high efficiency employed a high resistance transparent (HRT) layer inserted between the transparent conducting oxide (TCO) and the window layer, typically undoped tin oxide (TO). Kephart et al. [128] found that devices fabricated by depositing CdS:O directly onto fluorinated tin oxide (FTO) without an HRT layer suffered from poor $V_{oc}$, regardless of the thickness of the CdS:O layer. Using a similar FTO/CdS:O/CdTe architecture Gupta et al.[150] observed that improvements in current density were offset by losses in fill factor that was attributed to poor junction quality. The successful use of CdS:O requires careful optimization of sputter conditions, but high performance devices with power conversion efficiencies (PCE) ranging from 15.2–16.4% have been achieved independently by several groups [108, 128, 146, 151].

The trends discussed above have been well documented, but the underlying reasons controlling the observed behavior are not fully understood. It has been suggested that the catastrophic failure observed at high oxygen levels is caused by an excessive conduction band offset between the CdTe and CdS:O layers [128], while there are several possible explanations
for the improvements in $J_{sc}$ at moderate oxygenation levels. Changes in device performance could simply reflect the enhanced transparency of as-deposited CdS:O. Alternatively, CdS:O may decompose and release oxygen during subsequent high temperature processing, resulting in an intrinsic CdS layer of reduced thickness. Finally, as discussed above, the degree of interdiffusion with CdTe appears to be highly dependent on the amount oxygen in the window layer. The evolution of the window layer during device processing has been studied fairly extensively for CBD and evaporated CdS, but has not been examined in detail for CdS:O produced by sputtering. Moreover, to facilitate characterization previous studies of interdiffusion processes [144, 152, 153] have often employed structures and processes that are not representative of the superstrate architecture employed to produce high efficiency devices, potentially limiting their applicability.

In the conventional superstrate architecture, the CdTe absorber is deposited directly on CdS:O at high temperature (450–600 °C) by CSS or vapor transport deposition followed by an annealing step in the presence of CdCl$_2$ at $T \sim 400$ °C. These high-temperature, reactive environments likely cause significant changes to the underlying CdS:O material. For example, thermal annealing in an inert environment appears to convert CdS:O back to intrinsic CdS. Paudel et al.[127] varied the optical band gap of sputtered CdS:O films from 2.0–3.2 eV through manipulation of both oxygen content and substrate temperature. After annealing at $\sim 600$ °C in the He/O$_2$ ambient used during CSS all of these films exhibited similar properties that were characteristic of intrinsic CdS based on their crystal structure and band gap ($\sim 2.4$ 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 [128]. 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 layer 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 isolate the window layer in completed devices [154]. The first is a chemical etch that selectively removes CdTe, exposing the CdS surface. The second approach employs thermo-mechanical shock to cleave devices cleanly at the tin oxide/CdS interface. These complementary techniques expose the front and back side of the window layer, respectively, enabling facile characterization of window layer composition, structure, and opto-electronic properties. These tools are used to better understand the evolution of sputtered CdS and CdS:O window layers during both thermal annealing and device fabrication. It is shown that the changes induced by device processing are profoundly different than thermal annealing, and in contrast to conventional wisdom, the degree of Te interdiffusion and alloy formation is found to be enhanced when using CdS:O relative to CdS. These findings have significant implications for the understanding and future advancement of CdTe solar cells.

5.2 Materials and Methods

In this work the properties of un-oxygenated CdS are compared with moderately oxygenated CdS:O whose as-deposited band gaps are nominally 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 [148]. 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% O\textsubscript{2}/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/cm\textsuperscript{2} for CdS and CdS:O films, respectively, and the film thickness was fixed at 100 nm for device fabrication.

Samples were subjected to various additional processing steps. A subset of films were subjected to thermal annealing to provide a basis for comparison to both previous literature and samples that undergo full device processing. Thermal annealing of as-deposited CdS/CdS:O films was performed at 600°C for 5 min in an inert ambient. In device fabrication \( \sim 4 \) 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 CdCl\textsubscript{2} 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 \[116\]. In addition to complete devices, test structures were also used that were processed identically through CdCl\textsubscript{2} but did not have a back contact applied. All devices with CdS:O had very similar performance, yielding PCE’s of \( \sim 14\% \) as described previously \[148, 154\].

Two complementary techniques were used to isolate the window layers in completed devices: wet etch and thermo-mechanical lift-off. Both techniques have previously been applied to investigate the evolution of conventional CdS during device processing \[155, 156\]. Figure 5-1 displays schematics of the samples generated by etching (left) and lift-off (right). Selectively
etching of CdTe over CdS is challenging due to the chemical similarity of the two compounds. Mixtures of sulfuric and chromic acid have been used previously [155], but this has the drawback of employing hexavalent chromium. In this work a mixture of di-amine ethylene (DAE) and hydrogen peroxide was used to selectively remove CdTe [154]. DAE 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 of this technique for different materials is described below.

**Figure 5-1:** Schematics of the samples prepared by chemical etching (left) and thermomechanical lift-off (right).

Conventional mechanical lift-off techniques involve using epoxy to fixture the back of the device to another substrate, and then using brute force to pull the device apart [29]. Although this approach can be successful, the yield is poor and it is difficult to control with cleavage occurring at both the SnO₂|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 \((47, 49 \times 10^{-7}/K)\), which are significantly greater than the CTE of tin oxide \((38\times10^{-7}/K)\). After bonding an electron microscope mount (Ted Pella) to the back of a device using epoxy (Loctite 1c), the assembly was placed in liquid nitrogen. Upon immersion devices cleanly separate at the CdS-tin oxide interface without application of external force, and this 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 [154].

The composition, structure and optoelectronic properties of samples produced by these two techniques were quantified. Optical transmittance and reflectance were measured by an N&K spectrophotometer. The absorption coefficient \(\alpha\) was calculated using

\[
\alpha = \frac{1}{t} \ln\left(\frac{1 - R}{T}\right)
\]

where \(t\) is the film thickness, \(R\) is the reflectance, and \(T\) is the transmittance. Optical band gaps were determined using direct band gap Tauc plot analysis [58]. X-ray diffraction measurements were taken using \(\theta/2\theta\) and \(1^{\circ}\) glancing incidence scans from 20 to 70\(^{\circ}\) \(2\theta\) using Cu K\(\alpha\) radiation and a Rigaku Ultima diffractometer.

Dynamic SIMS was performed using an ION-TOF Model IV. Sputtering was carried out using 1 keV \(\text{O}_2\) 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 300×300 \(\mu\)m area. Analysis of a 100×100 \(\mu\)m area at the center of the sputter crater was performed using 25 keV \(\text{Bi}_3^+\) primary ions at a current of 0.4 pA. High resolution transmission electron microscopy (HR-TEM) was the tool used to investigate the detailed microstructure of a completed device employing 2.8 eV CdS:O cells using the facilities at Loughborough. TEM samples were prepared by focused ion beam (FIB) milling using a dual beam FEI Nova 600 nanolab. A standard \textit{in situ} lift out method
described previously [157] was employed for sample preparation. High-resolution TEM imaging was carried out in a FEI Technai F20 equipped with an Oxford Instruments X-Max 80 silicon drift detector (SDD) energy dispersive X-ray detector (EDX). EDX was used to produce chemical distribution maps of the cells as well as line scans and point analysis for quantitative elemental analysis. Acquisition and quantitative analysis of X-ray photoelectron spectroscopy (XPS) was performed by Charles Evans and Associates without sputter cleaning.

5.3 Results

The results for this chapter are presented in the following four sub-sections for clarity.

5.3.1 Etch selectivity, window layer consumption, and optical transformations

In this section, the selectivity of the chemical etch and the optical properties of window layers at different stages of device processing are compared. The etch chemistry is thought to preferentially attack oxygenated species, so experiments were performed to gauge its ability to selectivity etch CdTe while remaining unreactive to the underlying CdS and CdS:O. It was observed that this etch recipe completely removes the 4 µm CdTe films in ~90 s for beaker jacket temperatures between 10 and 50 °C, conservatively placing the CdTe etch rate (ER) at >2000 nm/min. The ER of as-deposited CdS and CdS:O films were then determined. The ideal etch selectivity for CdTe over CdS, \( S_{\text{CdTe/CdS}} \), is defined as

\[
S_{\text{CdTe/CdS}} = \frac{\text{ER}_{\text{CdTe}}}{\text{ER}_{\text{CdS}}}
\]

(5-3)

where \( \text{ER}_{\text{CdTe}} \) is the etch rate for CdTe and \( \text{ER}_{\text{CdS}} \) is the etch rate for the window layers. Figure 5-2 displays \( S_{\text{CdTe/CdS}} \) as a function of beaker temperature for 2.4, 2.8, and 3.2 eV CdS/CdS:O material. Window layer susceptibility to the etch varied greatly depending on the oxygenation level of the film and to a lesser extent bath temperature. Selectivities >300 were achieved for CdS sputtered in pure Ar across the 10–50 °C range explored. CdS:O films were much more
susceptible to the etch, and bath temperature was an important factor. The optimal 2.8 eV CdS:O enabled selectivities of 50–250, whereas highly oxygenated 3.2 eV CdS:O was limited to <50. The very high band gap CdS:O contains ~40 at. % O, primarily in the form of sulfate groups [148], and we speculate that CdSO₄ is more easily etched than CdS due to the greater oxygenation and bond ionicity. 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 at least 100, 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.

![Selectivity of etch recipe for CdTe over CdS for as-deposited CdS and CdS:O films as a function of bath temperature.](image)

**Figure 5-2:** Selectivity of etch recipe for CdTe over CdS for as-deposited CdS and CdS:O films as a function of bath temperature.

One potential consequence of device processing is that the effective thickness of the window layer 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
etching was measured by profilometry for the two samples at various stages of processing. To
improve the accuracy of these measurements test structures consisting of nominally 200 nm
CdS:O/CdTe bilayers deposited on glass were employed. Note that interdiffusion in normally
processed devices between TO and CdS is assumed to be negligible, so omitting the TCO and
HRT from these structures should not significantly alter the results [158, 159]. Figure 5-3
compares the thickness obtained after etching for the three samples after both thermal annealing
and device processing/etching. The bar chart reports the average thickness obtained from the
measurement of 5-8 step edges on each sample, with error bars capturing the variability
observed. The thermal anneal was found to have a negligible impact on film thickness in the case
of both CdS and moderately oxygenated CdS:O. However, fabrication and etching steps had
much more impact on the resulting thickness. In the case of intrinsic CdS there was a 13 nm
decrease after the processing steps and etching. In contrast, the thickness of the moderately
oxygenated cadmium sulfide was reduced 50 nm after processing/etch. It is suggested that
device processing alters the composition of the window layer adjacent to CdTe to make it
susceptible to the etch. These changes are significantly more pronounced in the case of CdS:O,
and the possible changes that may have occurred are discussed below.

The chemical etch allows the optical properties of the window layer to be examined after
device processing. The optical band gap of CdS and CdS:O window layers in the as-deposited
state, after thermal annealing, and from completed device stacks are compared in Figure 5-4.
As-deposited CdS had a slightly narrow band gap, perhaps caused by preferential sulfur
sputtering from the substrate [122]. After annealing, the band gap recovered to the
stoichiometric value of 2.4 eV. Thermal annealing had a similar effect on the moderately oxygenated CdS:O film, reducing its band gap from 2.8 to 2.4 eV. These findings are consistent with previous annealing studies of CdS:O [127, 128]. In contrast, the properties from both completed devices are significantly different, with the optical band gap being red-shifted to ~2.2 eV. In addition, it is notable that oxygenated material was red-shifted farther than the intrinsic material. The obvious difference between the two experiments is the exposure to Te in the fully processed devices, which presumably could lead to the formation of CdS$_{1-y}$Te$_y$ alloys. Using Eq. (5-1) the value of $y$ for the intrinsic and oxygenated cadmium sulfide after processing 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 [43].

Figure 5-3: Comparison of profilometry measurements of thickness of sputtered CdS and moderately oxygenated CdS:O as-deposited, after thermal annealing, and after fabrication and chemical etch for CdS/CdTe test structures on bare glass.
Figure 5-4: Optical band gap of window layers deposited on glass, after annealing in an inert ambient, and after complete device fabrication and etch for both intrinsic and moderately oxygenated CdS.

5.3.2 Structural transformations

Next, the structural response was determined using the same set of samples used to examine optical changes. Figure 5-5(a) displays the 1° glancing incidence XRD patterns of as-deposited and annealed CdS and 2.8 eV CdS:O films as well as the window layer in completed device stacks that remains after chemical etching. Glancing incidence scans were used to improve the surface sensitivity and prevent complications from the underlying tin oxide layer. Sputtered CdS without oxygen is a polycrystalline material that is highly oriented in the H(002) and/or C(111) direction, and it is difficult to distinguish these two peaks. Upon thermal annealing just 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 H(002) peak remains dominant. In contrast the 2.8 eV CdS:O is XRD amorphous as-
deposited, but upon annealing it undergoes recrystallization into the hexagonal phase, displaying a random orientation that is consistent with the powder pattern for this material. The pattern from the fully processed device is largely unchanged, though the intensity of the CdS peaks relative to the background is somewhat attenuated, possibly reflecting the thickness reduction discussed in the previous section. Note the as-deposited thickness in devices is 100 nm, so the 50 nm observed in surrogate samples would be significant. Neither sample exhibited diffraction peaks associated with CdTe after device processing, suggesting that the chemical etch completely removes the overlying CdTe layer.

To confirm these changes in structure, XRD was also used to analyze samples prepared by thermo-mechanical lift-off. Recall that the chemical etch exposes the window layer at the interface with CdTe, whereas the lift-off exposes the interface with TO (Figure 5-1). Figure 5-5(b) displays symmetric and 1° glancing incidence XRD scans obtained from the lifted off samples from devices with CdS and 2.8 eV CdS:O window layers. The wide angle scans are dominated by CdTe as expected, and even signal attributed to Au from the back contact is detected. However, glancing angle measurements reveal the presence of the hexagonal CdS phase, very similar to the patterns in Figure 5-5 that was detected in chemically etched samples. Notably tin oxide is not detected in these samples. Likewise, CdS is not detected in glancing angle measurements of the remaining glass/TCO superstrate after lift-off (not shown). These data suggest that the lift-off sample cleaved at the TO/CdS interface in a very clean manner. In addition, this thermo-mechanical cleavage approach was equally successful regardless of the level of oxygen in the as-deposited CdS layer.
Figure 5-5: X-ray diffraction patterns of (a) 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, and (b) symmetric θ/2θ and 1° glancing incidence scans of lifted portions after thermo-mechanical lift-off. Reference XRD patterns from [117, 160-162].
5.3.3 Secondary ion mass spectrometry

A powerful tool used in characterizing CdTe devices is secondary ion mass spectrometry (SIMS) [163]. Elemental profiles are gathered throughout the depth of the material. Previous SIMS analysis of CdTe devices have been profiles from the back contact, meaning several microns of CdTe layer must be removed prior to reaching the junction area and CdS layer. The sputter process used in 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 concentration gradients, the CdS layer is smeared out over a depth roughly three times larger than the estimated thickness as a result of the ever-expanding sputter volume [29, 163]. The techniques developed here enable the window layer in superstrate devices to be assessed without these complications.

Figure 5-6 displays SIMS profiles for selected elements obtained from both lift-off (left) and chemically etched (right) samples obtained from the same device fabricated with the optimal 2.8 eV CdS:O. Due to the absence of calibrated standards the intensity of each element is reported in terms of raw signal counts. The x axis was estimated by comparisons with SEM images. Figure 5-6(a) displays the SIMS profiles obtained from the two samples for sulfur and tellurium. As described above thermo-mechanical lift-off technique produces a very clean cleave at the CdS|TO interface, thus the beginning of the SIMS profile for this sample was placed at the CdS|TO interface (x = 0) and moves left into the CdTe layers. The profile for the etched sample was shifted horizontally so that the sulfur profiles overlaid in the window layer region. This places the start of this profile at ~x = -38 nm, and it proceeds to the right into the tin oxide. The identical shift applied to the S profiles 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 region that remains after the etching is only about half as thick as the lift-off sample, and this is attributed to the reduction in sample thickness observed during etching as described above. Recall that the thickness of the window layer in this sample was reduced ~50 nm after etching relative to the as-deposited or annealed material. Therefore, the lift off samples are most useful for providing analysis of the full window layer in completed devices. From the lift-off sample, it appears that the sulfur density is approximately constant in the layer adjacent to tin oxide and begins to decline near the interface with CdTe. The decline is initially gradual, becomes steeper at the interface between the two materials, and then the slope decreases again within the CdTe layer. Note that the sulfur content in CdTe is significant, on the order of an atomic percent. From the etched sample it is observed that sulfur declines exponentially as one moves into the tin oxide, and the signal becomes noisy suggesting that is reaching the limits of detection. This suggests that S diffusion into the TO is negligible as one would expect.

The tellurium profiles shown in Figure 5-6(a) show that significant interdiffusion occurs, and that there is a significant and stable amount of Te present adjacent to the interface with CdS. By comparing the Te signal intensity in the window layer with the bulk CdTe region the stable level in the window layer is consistent with the 5–10 atomic % levels extracted from the optical band gap assuming alloy formation. There is good quantitative overlap between the Te profiles obtained from the lift-off and etched sample. It is also consistent that the signal from the etched sample ends precisely where the Te content begins to increase sharply in the lift-off sample. The
**Figure 5-6:** (a) SIMS profiles of S and Te obtained from samples prepared using the thermomechanical 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 and move left into the CdTe layers, whereas the etched profiles begin at $x = -38$ nm and move right into the tin oxide.
chemical etch rapidly removes CdTe, so it is reasonable that this Te-rich interdiffused region would also be removed during etching.

Figure 5-6(b) compares the SIMS profiles of the major impurities (O, Cl, Cu) obtained from the two same samples. From the lift-off sample it is shown that the oxygen concentration is nearly constant throughout the window layer, and present in significant concentration. The intensity of the O signal coming from the window layer is only ~2.5 times less than the signal originating from the tin oxide layer (~67 at. %), indicating that significant levels of oxygen remain in the window region after processing. The O signal declines precipitously near the interface with CdTe, suggesting minimal diffusion into that layer. In contrast to sulfur and tellurium, there is a significant mismatch between the O profiles obtained from the window layer of both samples. One plausible explanation for the mismatch is that the chemical etch preferentially removes oxygen-rich areas of the window layer. As discussed above the etch is not selective to CdS:O with band gaps > 3 eV. This is further indication that the lift-off sample provides the more representative profiles of the full window layer in processed devices.

Chlorine is a critical impurity that is known to segregate to the window layer and Figure 5-6(b) compares the chlorine profiles obtained from the two samples. This is consistent with previous results showing preferential segregation of Cl to the window layer [157, 164]. The Cl profile from the lift-off sample does not align well with the etch sample. In fact in the etched samples the Cl profile has the inverse shape of the O profile, suggesting that the distribution of these two elements may be interrelated.

Copper plays a critical role in CdTe devices [165, 166], and it is introduced at the back of the device prior to or during metallization [116]. It is a fast grain boundary diffuser that can migrate during the annealing steps used to activate the back contact [167]. In particular is has
been found that Cu in CdS is detrimental to performance, and its accumulation in this layer has been suggested as a reason for device degradation [168]. SIMS is often used to understand the Cu distribution, but conventional profiling is performed from the back of the device, which limits its sensitivity in the heterojunction region. As shown in Figure 5-6(b) 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⁺ doubly ionized Te²⁺ [169]. However, if Te²⁺ was 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 signal is nominally identical in the etch sample in which the CdTe has been removed. Due to its importance in the device, the lift-off technique described here would be invaluable for understanding the accumulation of Cu and other impurities both as a function of device processing and after accelerated lifetime testing.

5.3.4 High-resolution transmission electron microscopy

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 elemental mapping were employed on a completed device. This device 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 as described previously [170], and had an efficiency of 16%. Figure 5-7 displays a high-resolution high angular annular dark field (HAADF) micrograph and concentration maps for chlorine, tellurium, oxygen, sulfur, and cadmium from a device cross section focused on the heterojunction region. From the HAADF
image the window layer is observed to be a contiguous layer, and from the distinct contrast it forms rather abrupt images with both the tin oxide and CdTe. To aid visualization 100 nm scale bars have been added to the HAADF image, and it is clear that the thickness of the window layer has been reduced, varying from 50–80 nm across the sample. The 50 nm that were 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.

Figure 5-7: HR-TEM image and associated elemental maps obtained from the heterojunction region of a completed device employing moderately oxygenated CdS:O.
The concentration maps contain a wealth of information on the spatial variation of elemental species throughout the layers. The color intensity scales with elemental concentrations, 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 [169, 171]. The Cl concentration appears to be significantly higher in the CdS layer than in the absorber, consistent with the SIMS profile. 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 oxygen map is very interesting. The base of the image shows the 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 that it is randomly distributed in clusters throughout the CdS. 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 visually detectable 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 in non-uniform within the window layer region. In fact, close comparison of these three elements show that regions of elevated O density are well correlated to regions where both the S and Cd signals are attenuated.

From these images it is hypothesized that oxygen segregates during processing, forming \( \text{SO}_4^- \)-rich domains and oxygen free CdS\(_{1-y}\)Te\(_y\) nanocrystals. A similar explanation was put forth by Kephart and co-workers[128] to explain their observed changes in optical properties during annealing. It is proposed that the chemical etch removes these regions of highly oxygenated
material, leaving CdS$_{1-y}$Te$_y$ nanocrystals. Compelling confirmation of this explanation is provided by SEM imaging and X-ray photoelectron spectroscopy. Figure 5-8 shows a cross-sectional SEM image of the etched sample used for SIMS analysis prepared using FIB. The layers present in this image glass, the CVD-deposited tin oxide bilayer, the remaining window layer, and the Pt cap introduced during sample preparation. In contrast to Figure 5-7, the window layer is no longer contiguous, but contains individual nanocrystals with several gaps. The thickness of these nanocrystals ranges from 30–100 nm. This is exactly the morphology one would expect if the O-rich regions shown in Figure 5-7 were removed.

**Figure 5-8:** Cross-sectional SEM image of a completed device employing moderately oxygenated CdS:O after removal of CdTe by chemical etching.
Figure 5-9 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 lift-off sample is almost exclusively in the form of sulfide groups (95%), with the residual sulfate signal being attributed to surface contamination as observed previously [148]. The discontinuous nature of the window layer after etching shown in Figure 5-8 was confirmed as a significant level of Sn was detected in the lift-off sample by XPS. Due to the high surface sensitivity one would not expect to observe Sn 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 5-9: High-resolution XPS spectra from the S 2p region obtained from the lift-off sample (red) and the etched sample (blue).
XPS also provided quantitative confirmation of the degree of Te interdiffusion seen in the SIMS and estimated by optical transmission. The lift-off sample was composed of a Te fraction of anions, or Te/(S+Te), equal to 0.22. This value is artificially inflated by the presence of sulfate complexes. This fraction in the etched sample 0.076, which very nearly matches the value inferred from optical band gap measurements. As described above the chemical etch rapidly removes CdTe, and it is presumed that it left the surface of the etched sample Te-poor.

5.4 Discussion

The two techniques introduced here provide unprecedented access to help understand the complex transformations that take place in the window layer during high-temperature CdTe deposition and annealing steps. The two isolation techniques provide different advantages. The primary benefits of the chemical etch is that it provides a means to assess the extent of consumption during processing as well as optical access to the window layer remaining after processing. One drawback is its imperfect selectivity, especially in CdS containing significant levels of oxygen and/or tellurium. The advantage of the lift-off technique is that it cleanly partitions the device at the SnO$_2$|CdS interface, leaving the window layer and heterojunction region intact for analysis.

The complementary nature of these two techniques coupled to the wealth of information provided by the suite of characterization tools has provided new insight into the evolution of the window layer during high temperature device processing. It is shown that the changes created by the reactive environment used in device processing are profoundly different than what occurs during thermal annealing. Moreover, this allows us to postulate the mechanism by which moderately oxygenated CdS:O improves CdTe device performance. Clearly the properties of the as-deposited material are not retained. During high temperature device processing the CdS:O
layer, initially 100 nm thick and amorphous, is transformed into a 50–70 nm thick film consisting Cd$_{1-y}$Te$_y$ nanocrystals and sulfate-rich domains. The optical band gap of this film suggests that this layer has a Te fraction approaches the solubility limit of 9–10 at. %, which was confirmed by XPS. This suggests that the alloying process is controlled by thermodynamics as opposed to transport limitations. SIMS profiling shows that adjacent to this homogenous region there is a layer characterized by strong S-Te interdiffusion, and it is postulated that some of this interdiffused region is removed by the chemical etch. Alloy formation is also observed in devices employing CdS, but the level of interdiffusion and the extent of recrystallization is reduced, and as such the reduction in the thickness window layer after processing is significantly less.

These observations contradict the prevailing opinion that the presence of oxygen within the CdS significantly inhibits interdiffusion and Cd$_{1-y}$Te$_y$ alloy formation [29, 145]. 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 favoring the hexagonal or cubic phase, respectively, though it is difficult to distinguish the two. In polycrystalline CdTe devices it is widely acknowledged that transport occurs predominantly through grain boundary diffusion [136, 143, 169], and as such the oxidation of these surfaces is a plausible mechanism to inhibit diffusion [145]. On the other hand, sputtered CdS:O is amorphous as-deposited, so it is reasonable to suggest that diffusion is significantly different, and perhaps more efficient.

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 [29, 145], but there is more than double that amount in sputtered CdS:O films yielding high performance devices, and as shown here a
significant fraction is retained in the window layer after processing. In sputtered CdS:O oxygen is present almost exclusively in the form of sulfate groups (SOₓ) [128, 148, 149], while in the case of CBD material it has been reported that O exists in substantially different forms including hydroxide (OH) [172], carbonate groups [173], and/or water[123, 173]. The role of oxygen may be indirect, creating the disordered, amorphous structure that promotes interdiffusion. However, 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 [169]. Likewise, McCandless and Sites [136] have 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 for CdTe deposition (600 °C). Many previous studies of interdiffusion have employed CdTe deposited at low temperature and/or used substrate configurations where the CdS is deposited onto the CdTe. In such studies processing temperatures did not exceed the ~400 °C level used during CdCl₂ treatment. The composition of the CdS₁₋ₓTeₓ alloy in completed devices approached solubility limits, suggesting that thermodynamics may be equally important as transport in controlling the evolution process. At 400 °C the maximum degree of tellurium alloying is just y ~ 0.025 [174], and as such the dramatic transformations described here would not be expected in devices employing low temperature processing.

The outstanding question that remains is how the physical changes described within manifest contribute to the improved Jₚc observed in device performance. There are basically two
possibilities. The first is that improvement in blue QE stem primarily from thickness reductions that overcome the bandgap narrowing associated with alloy formation. In addition, the sulfate-rich domains are expected to be transparent to visible radiation [128], and the microscopy images shown in Figures 5-7 and 5-8 suggest that this phase may account for 20-30% of the surface area, further enhancing the transparency of the window layer. The second reason is that unlike intrinsic CdS the CdS$_{1-y}$Te$_y$ alloy may have some degree of photoactivity that may contribute to current generation. To test these possibilities we compare the transmission of the window layer remaining after the chemical etch from one quarter of a completed device with the EQE from the identical sample as shown in Figure 5-10. There is generally good agreement from 300 nm until onset of the CdTe band edge at ~850 nm, supporting the thickness reduction argument. However in the 300-500 nm range the EQE is somewhat greater than the transmission, and perhaps photogeneration within the CdS$_{1-y}$Te$_y$ layer may be responsible for this discrepancy.

![Figure 5-10: EQE from a completed device as well as the transmittance from a sample from the same substrate after chemical etching.](image)

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The striking observations presented in this work have broad implications for the understanding of device physics in CdTe/CdS solar cells. The conventionally accepted band diagram of the CdS/CdTe heterojunction [175] assumes that the window layer in contact with the TCO is comprised of near-stoichiometric CdS with a band gap ~2.4 eV. In the case of CdS:O we show that the interface partner to tin oxide is a CdS$_{1-y}$Te$_y$ alloy with a ~2.2 eV band gap, followed by a graded layer to the CdTe absorber. The presence of the CdS$_{1-y}$Te$_y$ alloy may be the reason why the use of an HRT layer appears to be critical to obtain high efficiency devices when using sputtered CdS:O. It has been suggested that the TCO/CdTe$_y$S$_{1-y}$ junction is inferior to the standard TCO/CdS interface [176], and the insertion of the HRT layer may improve this junction by providing a more favorable band alignment [128]. Understanding the semiconductor properties of these CdTe$_y$S$_{1-y}$ alloys will be critical to both understanding current device technology and improving upon it. Clearly, additional work is needed to fully clarify these issues, and we expect the isolation techniques described here will be essential tools in those endeavors.

Finally, it is well known that impurities such as O, Cl, and Cu accumulate in the window layer region and can have a profound influence on device performance. Heretofore has been nearly impossible to examine this region in completed devices without the benefit of sophisticated techniques such as HR-TEM or atom probe tomography that require complicated sample preparation tools such as FIB that are time-consuming and expensive. The lift-off technique cleanly separates the device at the TO/CdS layer, leaving the window layer intact for characterization by profiling techniques such as SIMS, XPS, or Auger spectroscopies that can assess not just the presence of impurities but their bonding nature within the window layer. Though not the focus of the present study it is suggested that the lift-off technique provides a
powerful tool that could be used routinely to interrogate the nature of the heterojunction region as a function of processing conditions or to better understand its evolution during accelerated lifetime testing.

5.5 Conclusions

Two novel approaches for isolating the CdS window layer in completed CdTe solar cells have been introduced that are distinguished by their ease of execution, reproducibility, and the quality of isolation. The DAE etch provides a simple method for removing CdTe and uncovering the CdS back surface, and can be selective for intrinsic and moderately oxygenated CdS:O layers. The thermo-mechanical lift-off approach takes advantage of differences in CTE, and is highly complementary to the DAE etch in that it cleanly exposes the window layer at its interface with the tin oxide front contact. These techniques provide unprecedented access for characterization of the window layer in processed devices that can provide the fundamental insight required to advance the performance of CdTe solar cells.

These tools have been used to show that the optical and structural properties of the CdS:O layer are altered by the reactive environment of device processing in ways that are significantly different than thermal annealing. Both intrinsic and moderately oxygenated CdS:O are transformed into a ~2.2 eV band gap material, which is a nanocrystalline CdS$_{1-y}$Te$_y$ alloy as measured by XPS and SIMS profiling. A substantial fraction of oxygen remains through device processing, segregating into sulfate rich regions. In contrast to expectation, the degree of Te interdiffusion and recrystallization is significantly greater when using CdS:O relative to CdS, and it is suggested that differences in initial crystal structure may be the reason. Using CdS:O the CdS$_{1-y}$Te$_y$ alloy composition approaches solubility limits, suggesting the high temperatures used for CdTe deposition in this work drive the changes observed. Finally it is suggested that the
enhanced consumption of the window layer is the primary factor in the improved blue QE and efficiency observed experimentally.
CHAPTER 6

SUMMARY OF RESULTS AND RECOMMENDATIONS FOR FUTURE WORK

This chapter presents major results from Chapters 3–5 and recommendations for future work.

6.1 Summary of Results

This work focused on improving the processing and materials science of sputtered compounds employed in advanced front contacts of cadmium telluride (CdTe) photovoltaic devices. The primary materials of interest were the transparent conductive oxide (TCO) cadmium stannate (Cd$_2$SnO$_4$; CTO) and the window layer oxygenated cadmium sulfide (CdS:O). Each material was deposited by radio frequency (rf) magnetron sputtering, typically in a reactive ambient. Film properties were evaluated as a function of deposition ambient and post-processing. In the case of CdS:O, novel techniques were developed to enable characterization after completion of test structures and fully processed devices.

First, CTO deposition and annealing processes were investigated to establish the processing window for high-quality material and develop alternative fabrication configurations more amenable to large-scale manufacturing. The conventional process for producing CTO consists of sputter deposition followed by a contact annealing step in which the CTO film is placed in contact with a secondary CdS film. Using this conventional process, high-quality films with resistivity $\sim 2.2 \times 10^{-4} \ \Omega\cdot\text{cm}$ and transmittance $>90\%$ were produced when the sputtering ambient contained at least 20 volume % oxygen (balance argon) and the annealing temperature was 600–700 °C. Novel sputtering and annealing configurations were developed to bypass the conventional process. First, CdS layers from 5 to 30 nm thick were sputtered directly on the
CTO films. Second, annealing configurations using (1) contact with bare glass, and (2) no covering were developed. CTO/CdS bilayers annealed in the covered configuration had similar or better resistivity compared to the conventional process. Minimum resistivity ($1.9 \times 10^{-4} \ \Omega \cdot \text{cm}$) was measured for the bilayer with a 10 nm CdS layer, while use of excessive CdS (~30 nm) left residue after annealing. CTO and CTO/CdS bilayers annealed in the uncovered configuration had higher mobilities (~60 cm$^2$/V-s) but were more resistive ($\sim 3 \times 10^{-4} \ \Omega \cdot \text{cm}$) due to lower carrier concentration. Their properties were fairly independent of the CdS thickness. These results suggest that cadmium supplied by either the contact anneal or through a secondary layer is necessary to minimize resistivity through increased carrier concentration. The most scalable process, CTO-only deposition and uncovered anneal, suffers a penalty of only ~50% of the minimum resistivity. CdTe devices employing annealed CTO/CdS bilayers had as good or better efficiency compared to those using the standard proximity anneal.

Next, CdS:O window layers were deposited and correlated to device performance holding all other parameters constant. Simple variation of the sputtering ambient composition (oxygen/argon) produced films with drastically different properties. Oxygen was incorporated in the films at up to ~45 atomic % in the form of SO$_x$ groups. Films were polycrystalline when sputtered in ≤1% oxygen, and were XRD-amorphous in ambients containing more oxygen. The optical band gap increased monotonically from its intrinsic value of 2.4 eV to as high as 3.8 eV for a 10% oxygen/argon ambient. All secondary device parameters ($V_{OC}$, $J_{SC}$, FF) improved with the addition of oxygen up to 6% in the ambient, with the maximum efficiencies reaching >14%. Devices incorporating a CdS:O layer with an excessive oxygen-containing ambient had lower efficiency, and exhibited loss of rectifying behavior at 9% addition. In addition, the devices exhibited a monotonic increase in blue quantum efficiency (QE) with increasing oxygen in the
sputtering ambient up to the optimum, and reduced red QE for excessive oxygen. Measurements of the valence band energy levels suggest that the cause for catastrophic failure at 9% oxygen is excessive conduction band misalignment at the CdTe/CdS interface, which creates a barrier to electron transport. The CdS:O process was scaled up to two larger deposition systems. For the device architecture and processing employed in this work, the optical band gap of CdS:O was found to be a useful metric for process transfer and reproducibility. It was found that CdS:O with an optical band gap of 2.8 eV yielded similar high efficiency (>14%) devices using three different sputter tools and multiple sputter targets, though the specific sputter conditions varied with both system and target. Replacement of conventional chemical bath deposited CdS with sputtered CdS:O was a key factor that enabled the efficiency of CdTe devices fabricated on ultra-thin Willow glass to be elevated from 14.1% to an NREL-certified value of 16.4%, the current world record for a flexible CdTe photovoltaic cell.

The final contribution was advancing the understanding of how the window layer composition and properties evolve during exposure to the high temperature, reactive environments employed in subsequent device fabrication. To this end two relatively simple techniques were developed to expose the window layer in fabricated devices. A liquid chemical etch consisting of water, hydrogen peroxide, and di-amino-ethylene was used to selectively remove CdTe, leaving the underlying glass/TCO/HRT/CdS stack intact for characterization. Second, a thermo-mechanical lift-off was used to cleave the device at the HRT/CdS interface. Subsequent characterization was performed on films, test structures, and devices with CdS and the optimal CdS:O layers. The as-deposited CdS window layer had an optical band gap of ~2.3 eV and was polycrystalline with a single reflection, whereas the CdS:O material had a 2.8 eV band gap and was amorphous. Thermal annealing of both window layers resulted in a shift in
band gap to 2.4 eV and a small amount of recrystallization to the hexagonal CdS phase. However, device processing through CdTe deposition and CdCl$_2$ annealing steps, the optical band gaps further narrowed to ~2.2 eV and there was increased recrystallization. Remarkably, the CdS:O material exhibited a lower band gap and greater recrystallization than the CdS one. In addition, consumption caused by fabrication steps and etching was four times greater in the CdS:O case compared to CdS, whereas thermal annealing had very little effect on thickness. SIMS and cross-sectional microscopy were used to corroborate these results. SIMS tellurium depth profiles were in qualitative agreement with the optical data, suggesting that as much as 5–10 at. % was present in the final window layer. In addition, it was shown that the thickness of the window layer was reduced significantly by the chemical etch, whereas the lift-off provided an intact sample for analysis that begins cleanly at the interface with tin oxide. Substantial amounts of oxygen (~10 at%) are retained in the window layer after device processing, and critical impurities such as Cl and Cu were found to preferentially segregate to the window layer.

Further validation was provided by TEM cross-sectional microscopy coupled to elemental analysis by EDAX. It was shown that the window layer thickness was reduced from 100 nm in the as-deposited state to ~70 nm in the final device, and that oxygen was found to be segregated in O-rich clusters, presumably sulfate. Comparison to microscopy imaging of the window layer after etching suggested that these O-rich domains are removed by the etch, leaving a discontinuous layer of CdS$_{1-y}$Te$_y$ nanocrystals, whose composition as measured by XPS is in good agreement with the values extracted from the optical band gap. Overall, the transformation in window layer properties includes optical band gap narrowing, recrystallization, and layer thinning/consumption caused by sulfur/tellurium interdiffusion. The oxygenated window layer has a higher final tellurium content and is consumed more than the un-oxygenated one. These
results explain the device QE trends from the previous chapter, in which the blue QE increased monotonically with oxygen content in the window layer. Furthermore, this work provides a convincing argument that thermal annealing is a poor proxy for device fabrication steps. These results significantly alter the conventional understanding of the nature of the heterojunction, which presumed that the presence of O inhibits interdiffusion. While fully addressing this question is beyond the scope of this thesis, the unprecedented access to the heterojunction region in completed devices enabled by the techniques developed herein is a powerful tool for the community to advance the fundamental understanding of device physics.

6.2 Recommendations for Future Work

The following subsections outline future work areas that would provide an extension of this work and/or are suggested by results from this work.

6.2.1 Fundamental understanding of the heterojunction region in CdTe devices

The isolation techniques developed in Chapter 5 provide access to the front and back surfaces of the window layer and enable powerful depth profiling and thin-film characterization, respectively. Characterization performed in this work is preliminary in nature and limited in scope to sputtered CdS:O window layers and high-temperature close-space sublimation deposited CdTe absorbers. Future work is recommended to identify the oxygen-containing grains in the window layer, extend the analysis to un-oxygenated CdS and highly oxygenated CdS:O, and develop an improved understanding of the heterojunction in completed devices.

First, the bonding and crystallinity of regions with retained oxygen could be determined using selected area electron diffraction inside of a transmission electron microscope. Assuming that these oxygen-containing regions have some degree of crystallinity, the resulting diffraction pattern would be used to determine the lattice spacing. By comparing the obtained lattice
spacing to those determined from published X-ray powder diffraction studies, an indisputable chemical structure could be identified.

Next, the SIMS depth profiling, XPS bonding states, and cross-sectional TEM analyses performed on the optimal CdS:O material should be performed on un-oxygenated CdS and highly oxygenated CdS:O. While the $J_{SC}$ increase in devices incorporating optimal CdS:O material was explained based on the analysis in Chapter 5, it is unclear why there were also gains in $V_{OC}$ and FF compared to CdS. Oxygen in the optimal material was credited with increasing interdiffusion, but does it also passivate parasitic defects at the junction or are the improvements primarily caused by better conduction band alignment at the CdS/CdTe interface? At the opposite extreme, catastrophic failure was observed in devices employing highly oxygenated CdS:O. This material is more difficult to analyze by the chemical etch technique developed here because of its high etch rate. However, it too most likely undergoes transformations during the device processing steps. Analysis of this material would uncover these transformations and confirm/reject the conduction band alignment argument presented in Chapter 4. Moreover, by characterizing the final material, it should become more obvious why the optimal and highly oxygenated CdS:O materials behave so differently in the device and perhaps even lead to a simple method for determining when a film is too oxygenated for use in high-performance devices.

Last, the procedure for determining the band structure of individual layers and band offset at interfaces presented in [177] should be applied to fabricated devices incorporating intrinsic CdS, moderately oxygenated CdS:O, and highly oxygenated CdS:O window layers. Certainly, one would expect the obtained data to differ somewhat from those presented in Chapter 4 of this work, which used as-deposited XPS and optical data combined with
assumptions of constant work function and Anderson’s rule for band offsets. As discussed in Chapter 4, the nature of the conduction band offset at the CdS/CdTe interface is critical to the device photo-voltage and electron transport. Further inquiry would answer whether the improved voltages in devices with CdS:O layers presented in Chapter 4 were a result of a more desirable conduction band offset at the junction or if another phenomenon controls this trend. Furthermore, confirmation that the catastrophic failure in devices with highly oxygenated CdS:O is caused by excessive conduction band alignment would prove valuable. At this time, it is unclear whether structure, chemistry, or energetics are primarily responsible for this behavior.

6.2.2 Incorporate CdS:O window layer in substrate thin-film PV devices

CdS window layers are used in other thin-film PV devices, such as those based on copper indium gallium diselenide (CIGS) and copper zinc tin sulfide (CZTS) absorbers. Unlike high-performance superstrate CdTe devices, these devices use the substrate architecture, in which the device stack is deposited in opposite order. In substrate devices, the window layer is not exposed to high-temperature processing. The high band gap sputtered CdS:O material presented in Chapter 4 would presumably retain its as-deposited properties in these devices and offers reduced parasitic absorption compared to CdS. These technologies currently favor chemical bath deposited CdS or ZnS window layers, most likely to avoid sputter damage to the absorber surface. There are a number of processing strategies which may be utilized to reduce damage caused by highly energetic charged particles in the sputtering process, such as the use of substrate biasing, higher ambient pressure, and lower power.

6.2.3 Alternative window layers

Results presented in Chapter 5 suggest that the wide band gap CdS:O window layers transition to a narrow gap CdSTe material during high-temperature CdTe deposition and
annealing steps. Owing to its optical band gap of ~2.2 eV, the final material parasitically absorbs a significant fraction of incident light. Establishing an alternative window layer or front contact stack that maintains or improves junction formation with CdTe and has a higher band gap than CdS could enable significant J_{SC} gains.

One material that has potential to improve the front stack is zinc sulfide (ZnS), another II-VI material with a wide band gap of ~3.6 eV [178]. Simple substitution of ZnS for CdS has not been successful in CdTe devices due to conduction band misalignment and difficulty in doping ZnS [106]. Substitution of the alloy CdZnS for CdS could enable the formation of a stable wide band gap window layer. Interesting window layers to fabricate include ZnS/CdZnS/CdS, ZnS/CdZnS, CdZnS/CdS, and CdZnS. Indeed, a device with a CdZnS/CdS structure was fabricated with an efficiency over 15% [179]. Alloyed CdZnS layers can be produced either through co-sputtering of CdS and ZnS or as a result of the high temperature CdTe deposition/anneal processes. Because zinc diffusion to the junction may significantly worsen device V_{OC} and FF [106], lower temperature CdTe deposition may be required. Other materials worth considering are metal oxides with optical band gaps >2.6 eV, such as indium oxide, zinc oxide, and gallium oxide.
REFERENCES CITED


APPENDIX A

OPERATION OF THE HIDEN EQP 500 ATTACHED TO THE SPUTTER-PLASMA DIAGNOSTIC SYSTEM FOR CHARACTERIZING SPUTTER PLASMAS

This appendix describes work performed with the Hiden EQP 500 mass spectrometer in the Sputter-Plasma Diagnostic system [180] to characterize rf magnetron sputter plasmas of II-VI materials.

A.1 System Description

The Sputter-Plasma Diagnostic (SPD) Tool is a system integrating a high-vacuum sputtering chamber with a Hiden EQP 500 quadrupole mass spectrometer. The system is currently equipped to sputter thin films and analyze the energy and mass spectra of residual gases and sputtered neutral and charged particles. Figure A-1 displays a schematic of the system. The chamber accommodates up to six sputter guns in sputter up configuration and has a base pressure of $\sim 1 \times 10^{-9}$ Torr after bake out. Two turbomolecular pumps are used to evacuate the chamber and spectrometer with minimal contamination. The mass spectrometer is differentially pumped. For typical process conditions at $\sim 1 \times 10^{-2}$ Torr in the main chamber, the pressure is $\sim 1 \times 10^{-7}$ Torr in the spectrometer. The EQP is mounted to the chamber via a rotating flange. The spectrometer orifice is often placed in direct line of sight of the sputter plasma during analysis.

Figure A-2 displays a computer-aided drawing of the Hiden EQP 500. Particles enter through the orifice. An ion source, energy filter, and quadrupole mass filter are used to ensure that only a desired subset of particles reach the detector for counting. A series of electrostatic fields move ions downstream of the ion source. The energy filter is a $45^\circ$ electrostatic sector field that transmits ions within a narrow energy range. The quadrupole mass filter consists of
three stages. Each quadrupole contains four rods in a diamond pattern: two opposing rods are DC biased while the remaining two are AC biased at radio frequency. Only ions with the correct mass-to-charge ratio have the required trajectory to pass through the filter. Finally, the ions impact the secondary electron multiplier detector. Collision with the semiconductor coated detector wall causes secondary electron emission. Subsequent avalanche collisions are caused by the curved geometry of the detector and the high applied voltages. At the end of the detector, an anode collects and counts incident electrons.

A.2 Modes of Operation

The four basic modes of operation are classified by whether the ion source is on or off and whether the internal electrostatic fields are set up to detect positive or negative ions. The unit is in residual gas analysis (RGA) mode when the ion source is on, while it is in secondary ion mass spectrometry (SIMS) mode when the ion source is off. Typically, RGA mode is used
for analysis of neutrals, whereas SIMS mode is used to analyze plasma-generated ions. In RGA mode, neutral particles diffusing into the orifice are ionized by electrons emitted from a filament in the ion source. Operation in RGA and SIMS modes is the same downstream of the ion source. On the other hand, electrostatic fields have opposite charges for positive and negative modes. Positive RGA mode uses electron impact ionization to create positively charged ions, whereas Negative RGA mode uses electron attachment ionization to create negatively charged ions.

A.3 Major Scan Types

Scans are performed using Hiden’s MASsoft software and are differentiated based on the choice and/or increment of the dependent variable. The first major scan type is a mass spectra scan, which plots the relative abundance of species within a range of mass-to-charge ratios. These scans are commonly used for residual gas analysis of the chamber and to semi-quantitatively calculate the relative abundance of species. The Bar scan in MASsoft performs a mass spectra scan at each whole number value for m/z. This is the best option for quick

Figure A-2: Computer-aided drawing of the Hiden EQP 500 mass spectrometer. Adapted from an official Hiden Analytical Ltd. publication [181].
qualitative scans. For quantification, the Profile scan should be used, where the m/z increment can be set from 0.01 to 1. Figure A-3 shows an example Positive SIMS Profile scan in the range of the five zinc isotopes during sputtering from a ZnS target. The relative abundance of the isotopes is well known and provides a fingerprint of the element. Minor isotopes are commonly used for quantitative analysis when mass interferences are present with the major isotope. In this case, $^{64}\text{Zn}$ has a potential interference with $^{64}\text{S}_2$.

![Figure A-3](image)

**Figure A-3:** Positive SIMS Profile scan in the m/z range 63–71 amu during rf magnetron sputtering of ZnS.

The second major scan type is the ion energy distribution scan. This displays the energy distribution of particles as they enter the orifice. These scans provide information on the dynamics of the sputtering process and enable calculation of fundamental parameters such as the ion temperature and plasma potential. An example plot of $^{66}\text{Zn}$ during ZnS sputtering is shown.
in Figure A-4. As expected, the arrival energy decreases with increasing pressure due to the lower mean free path.

**Figure A-4:** Ion energy distribution scans of the $^{66}$Zn isotope during rf magnetron sputtering of ZnS at different processing pressures.

The third major scan type is the ionization potential scan. This scan plots the abundance of ions as a function of the ion source electron potential (termed Electron Energy in the MASsoft software). Figure A-5 shows an ionization potential scan for argon in the plasma off condition. This plot can be used to calibrate the Electron Energy variable to the known ionization potential for argon (15.6 eV).

**A.4 Unresolved Issues**

This section describes a few of the most serious problems with the tool that have yet to be solved.
A.4.1 Undesirable fluorocarbons in residual gas

Scans of the residual gas in Positive RGA mode were commonly performed to obtain qualitative information on the external constituents presents in the chamber. Figure A-6 shows one such scan. Some species, such as $\text{N}_2$ and $\text{H}_2\text{O}$, are observed in most UHV chambers due to leaking and backstreaming. On the other hand, fluorinated compounds seen in this figure are contaminants caused by off gassing from either a vacuum grease/oil or the Teflon seal on the rotating flange. The intensity for these compounds is fairly low, so the simplest workaround is to simply produce much higher intensity in the desired compounds. At typical intensities ($10^5$–$10^6$ c/s), the contaminants make up less than 1% of the signal.

A.4.2 Unable to detect sputtered neutrals

The second unresolved issue is the inability to detect neutral sputtered particles. Sputtered particles are generally composed of 99% neutrals and 1%, and thus make up a very
important part of the sputtered particle population. While the instrument has been used to analyze neutrals in the residual gas as well as sputtered ions, neutral constituents of the sputtering target have not been detected. In the case of ZnS, atomic and molecular Zn- and S-containing species are not detected in Positive RGA mode. Figure A-7 shows that the residual fluorinated compounds are readily detected during sputtering, but sputtered Zn neutral particles are only present at very small levels. Simple modifications, such as altering the process pressure/power and target-to-orifice distance, did not significantly change the observed detection.

Assuming that there is a large generation of sputtered neutral particles, one or more mechanisms is preventing them from being counted by the EQP. A large fraction of particles will collide with and stick to a surface instead of being sampled due to the small solid angle from

\[ \text{Figure A-6: Positive RGA mass spectra of residual gas. Fluorocarbon compounds are shown in red.} \]
the target to the 100-µm diameter orifice. Particles that do enter the orifice may impinge on the hot filament or have too large of an arrival energy for passage through the sector field.

**Figure A-7:** Positive RGA mass spectra for 62–70 amu during ZnS sputtering. Fluorocarbon compounds in the residual gas have a much larger signal than atomic zinc.
APPENDIX B

DETAILED SPUTTER DEPOSITION PROCEDURES

In this appendix detailed procedures are provided for the three sputter systems discussed in Sections 2.1.1, 2.1.2, and 2.1.3.

B.1 CVC SC-3000 Sputter Tool Procedure

The general deposition procedure is outlined here. Fill the liquid N\textsubscript{2} cold trap reservoir beforehand using a 56-gal dewar. With the system vented and open, place a substrate in the substrate holder prior to fixturing using four corner screws. Manually position the shutter between the target and substrate in preparation for pre-sputtering. Next, fixture the open top metallic cylindrical shell around the deposition area using the top screw. Pull the bell jar into position such that the rubber gasket sits symmetrically on the lip of the metallic bottom section flange. Using the digital interface, select Backing Valve Off on the Pump Valves screen to close the valve between the roughing and diffusion pumps. Next, select Roughing Valve On in the Pump Valves area. The roughing pump is now pumping on the chamber. When the pressure reaches \~100 mTorr on the MKS Baratron PDR-C-1C readout, select Roughing Valve Off followed by Backing Valve On. The roughing pump is now backing the diffusion pump. Meanwhile, the chamber pressure will creep up. Wait for the foreline pressure to drop below 50 mTorr, as indicated by a Materials Research Corporation multi-gauge readout. Slowly open the manual gate valve. The diffusion pump is now pumping on the chamber. Turn on the ion gauge. Once the base pressure is satisfactory, turn off the ion gauge. Although the ultimate pressure is \~1\times10^{-7} Torr, base pressures of 2\times10^{-6} Torr were commonly used. Introduce the ambient gas into the chamber using the MFC screen on the digital interface and set the flow rates using the MKS four-channel readout. Quickly close the gate valve to increase the ambient pressure and
turn on the match network controller. Start the rf power supply. The default ignition power was 50 W. When sputtering at higher power, the power setting was slowly ramped up after ignition. Verify that a plasma has been ignited. Adjust the gate valve to achieve the desired pressure (downstream operation). Start the QCM controller timer. This deposition on the shutter is known as pre-sputtering, and is used to remove contamination on the target surface. Next, simultaneously open the shutter, zero the QCM, and restart the QCM timer. The thickness reported by the QCM is a proxy for the actual film thickness. Calibration is performed through a simple proportional relationship. When the deposition is completed, close the shutter and stop the QCM timer. If necessary, ramp down the power before turning off the power supply and match network controller. Turn off MFC valves using the digital screen. Finally, close the gate valve. The pumps are now in a safe state, with the roughing pump backing the diffusion pump and the gate valve closed. To collect the substrate, vent the system from the Purge/Vent page of the digital screen, lift up the bell jar, and remove the screws from the sample holder.

B.2 Kurt J. Lesker CMS-18 Sputter Tool Procedure

A general deposition procedure is given here. The chamber should be under high vacuum and the load lock should be vented. Place the substrate on the holder and load into the load lock transfer arm. Close the load lock lid and initiate the Pump LL recipe in the software. The valve behind the chamber turbo pump is closed to protect backflow into the chamber. The load lock turbo pump begins ramping up once the roughing pump brings the load lock to low vacuum. After waiting for the load lock to pump down to within about 1 order of magnitude of pressure with the chamber, start the Sample Load recipe. This step is not completely automated. The program walks the user step by step through the necessary manual operations. The gate valve between the load lock and chamber opens. Next, the user operates the manual load lock
arm to extend the sample into the chamber. A substrate manipulator mounted to a motor is raised to a pre-defined height, termed the transfer position, to pick up the sample holder from the load lock chamber sample holding apparatus. The load lock arm is manually withdrawn, and the manipulator is placed at the desired position. Now, the software closes the load lock-chamber gate valve. The Sample Load procedure typically causes the chamber pressure to rise slightly due to the higher pressure in the load lock. Press the Run Recipe button in the software once the chamber pressure is acceptable. Common base pressures in this work were ~1×10⁻⁷ Torr. Next, select the desired recipe from the list. The deposition sequences are fully automated and are briefly outlined as follows. The gate valve is partially closed to reduce the pumping speed. Ambient gas is added to the chamber at ~100 mTorr. The rf power supply and matching network are turned on. If necessary, the rf power is ramped up slowly from an initial value of ~50 W. Sample rotation commences at a predefined rotational velocity. Pre-sputtering against the target surface is performed to reduce contamination. The target and substrate shutters are opened at the beginning of the deposition time. At the end of the deposition time, the shutters are closed, the rf power is turned off, and gas flow is stopped. To retrieve the sample, run the Sample Unload and LL Vent recipes.

**B.3 Unifilm PVD-300 Sputter Tool Procedure**

The general deposition procedure for sputtering a thin film using the rf power supply is listed here. Similar procedures apply to DC sputtering and ion beam etching processes. The chamber and load lock should be under vacuum. On the CPU touch screen, navigate to the Load Lock screen. Touch on the desired planet such that it is highlighted in red and indicates a Load step will be performed. The planetary assembly rotates such that the desired planet is in front of the load lock and the load lock is vented. During this time, place the substrate on a 3-in diameter
aluminum platen. Open the load lock and place the platen in the fixture. Close the load lock to initiate pumping. Follow the on-screen instructions to load the platen on the planet. Navigate to the deposit screen and enter information for the run. Once prompted, initiate ambient gas flow. Use the throttle toggle switch and hand-operated adjustment knob to set the chamber pressure. Start the rf power supply and matching network. After entering the required information on the touch screen, push Start Run. The run sequence will automatically shut off the rf power once the requisite time has passed as input by the user. Turn off the matching network and ambient gas flows. Set the throttle toggle switch to off. Navigate to the Load Lock screen. Set the used planet to Unload. Follow the on-screen instructions to pick the platen off the planet and place in the load lock. Next, the load lock is vented and the platen and substrate are retrieved. Close the load lock to initiate pumping.
APPENDIX C

SECONDARY AUTHOR CONTRIBUTIONS

I was a co-author on the following peer-reviewed journal articles. Here I provide the citations and a brief description of my contribution to these efforts.


   This article showcases a then-world record flexible CdTe solar cell fabricated on Corning’s Willow glass. My contribution was to fabricate thin-film layers used in devices, including cadmium stannate front contacts which were ultimately not used in the highest performing cells.


   This article reports optical transitions in CdTe devices using photocapcitance and photocurrent techniques. My contribution was to fabricate a subset of the devices used in the study.


   This article reports a new world-record flexible CdTe solar cell fabricated on Corning’s Willow glass. One of the primary advances in this work compared to the 2014 APL article is the
use of a sputtered CdS:O window layer, as described in Chapter 4. My contributions included incorporating CdS:O into devices and performing device optimization studies on this layer.
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