Earth-abundant Cu$_2$BaSnS$_4$ (CBTS) thin films exhibit a wide bandgap of 2.04–2.07 eV, a high absorption coefficient $>10^4$ cm$^{-1}$, and a p-type conductivity, suitable as a top-cell absorber in tandem solar cell devices. In this work, sputtered oxygenated CdS (CdS:O) buffer layers are demonstrated to create a good p–n diode with CBTS and enable high open-circuit voltages of 0.9–1.1 V by minimizing interface recombination. The best power conversion efficiency of 2.03% is reached under AM 1.5G illumination based on the configuration of fluorine-doped SnO$_2$ (back contact)/CBTS/CdS:O/CdS/ZnO/aluminum-doped ZnO (front contact).

1. Introduction

Earth-abundant and air-stable thin-film materials are regarded as one promising option to meet the increasing demand for low-cost solar cell manufacturing. Earth-abundant Cu$_2$BaSnS$_4$ (CBTS), crystallizing into the trigonal symmetry with a space group of either P3$_1$, P3$_2$1, or P3$_3$1,[1,2] has emerged as a promising low-cost solar energy material and has attracted the attention of the academic community. Its noncentrosymmetric crystal structure, along with the large atomic size differences among the constituent cation elements, endow CBTS with more beneficial defect properties for efficient photovoltaic and photoelectrochemical solar energy conversion than kesterite Cu$_2$ZnSnS$_4$ (CZTS).[3,4] Its wide bandgap, $E_g = 2$ eV,[4,5] is suitable as a top-cell absorber in a tandem solar device. Tandem solar devices generally consist of two or more stacked subcells, whereby the top cell absorbs only the blue light of the solar spectrum leaving the red light to pass through and be absorbed by the bottom cell. Thus, the top-cell absorber calls for a wide bandgap of 1.7–2.1 eV to enable the red light to transmit, whereas the bottom-cell absorber should have a narrow bandgap of 1.0–1.4 eV to ensure that the red light can be absorbed.[6] According to the Shockley–Queisser theory, a maximum power conversion efficiency (PCE) of $\approx 22\%$ is attainable for a CBTS ($E_g = 2$ eV) single-junction solar cell; if CBTS could serve as a top cell in series with an Si ($E_g = 1.1$ eV) bottom cell, the total PCE of the tandem device could be greatly boosted up to $\approx 34\%$, outperforming the single-junction solar cells.[7]

CBTS is an intrinsic p-type semiconductor owing to Cu-deficiency,[8] hence it requires an n-type partner material to form heterojunction for solar cell devices. As shown in Figure 1, CBTS has a very large lattice constant; therefore, it is difficult to find suitable heteropartner materials to make ideally lattice-matched junctions. Misfit dislocations may produce dangling and wrong bonds at the interface that may create deep trap states. Via these trap levels, the photogenerated holes and electrons can recombine at the heterointerface, which could be even more detrimental to open-circuit voltages ($V_{OC}$’s) than recombination in the absorber bulk for wide-bandgap solar cells.[9–11] Among the conventional buffer materials shown in Figure 1, CdS, with a bandgap $E_g = 2.4$ eV, appears to show the smallest lattice mismatch with most of the absorbers. Also, with a suitable conduction band alignment to other absorbers and to transparent conductive oxides (TCOs), CdS is well known as a typical n-type heteropartner material, which is usually called the ‘buffer layer’ in Cu(In,Ga)Se$_2$ and CZTS solar cells or the ‘window layer’ in CdTe solar cells.[12,13] However, blue light with photon energies $E > 2.4$ eV is strongly absorbed by the CdS layer and so does not contribute to the photocurrents. This is evident by the reduction in the external quantum efficiency (EQE) with the spectral wavelength $\lambda < 520$ nm for most solar cell devices using a CdS buffer or window layer. Reducing the thickness of the CdS layer can minimize this absorption loss of blue light, but can increase the density of pin holes. The increased pin hole density may give rise to direct contact between the TCO front contact and the absorber layer, causing weak diodes and degrading device performance. An alternative approach is to increase the bandgap of CdS via reactively sputtering a CdS target in a mixed O$_2$/Ar environment. In addition to an increase in bandgap, oxygenation may cause a reduction in grain size and crystallinity, ultimately resulting in a nanocrystalline or even an amorphous film and a dramatic increase of the film resistivity.[13–18] Notably, oxygenation can upshift the conduction band minimum (CBM) compared to that of CdS, keeping the electrons away from the Fermi level, which therefore serves to reduce the effective interface recombination rate.
between the CdTe and the window layer.\(^{[13]}\) The as-deposited oxygenated CdS (CdS:O) layers are usually not a single phase of a CdS\(_{x}\)O\(_{1-x}\) but rather a mixture of CdS, CdSO\(_{4}\), and CdSO\(_{3}\) phases.\(^{[11,15-19]}\) The highly resistive CdSO\(_{4}\) phases can also act as passivators of the misfit CdTe/CdS interface.\(^{[13,18]}\) Hence, surface passivation along with reduced interface recombination rates by using CdS:O window layers ensure high \(V_{OC}\)'s for CdTe solar cells.\(^{[13]}\) However, CdS:O layers have not been evaluated for Cu-based chalcogenide solar cells.

In this work, we prepared CBTS films by post-sulfurization of cosputtered sulfide precursors on fluorine-doped SnO\(_2\) (SnO\(_2\):F, FTO) coated glass substrates. FTO is a TCO that is quite stable at high temperature annealing \(T > 600 ~\text{°C}\). Thus, FTO can serve as a good transparent electrode for top-cell purposes. We demonstrate CBTS-based polycrystalline thin-film solar cells with improved \(V_{OC}\)'s (0.9–1.1 V) by incorporating n-type CdS:O buffer layers, where CdS:O layers were deposited by reactively sputtering a CdS target under conditions of varying O\(_2\)/Ar flow ratios. As is well known, obtaining \(V_{OC}\) greater than 1 V is quite challenging for the single-junction thin-film solar cell. To date, \(V_{OC}\) values exceeding 1 V have only been reached in CdTe,\(^{[20]}\) Cu\(_2\)O\(_3\),\(^{[9]}\) and organic-inorganic lead halide\(^{[11,21]}\) based solar cells. Our results suggest that CBTS is a promising wide-bandgap absorber material enabling high \(V_{OC}\)'s in the top cell for tandem solar cells.

2. Results and Discussion

Figure 2a inset shows the top-view scanning electron microscope (SEM) image of a sulfurized CBTS film deposited on an FTO coated glass substrate. It is seen that this ~2 \(\mu\)m thick film is pinhole-free and compact without any obvious secondary phases, properties of which are preferred for solar device applications. Energy dispersive X-ray spectroscopy suggests that the sulfurized CBTS film has a Cu poor composition with the atomic ratios of Cu/(Ba+Sn)=0.86. This sulfurized CBTS film additionally shows a high crystallinity as evident from the X-ray diffraction (XRD) pattern in Figure 2a. All the observed XRD reflections agree well with the experimental values of trigonal CBTS (red bars) reported by Teske and co-workers (i.e. PDF 97-005-2685, space group \(P3_1\)).\(^{[21]}\) Our CBTS film exhibits a dominant \(\{110\}\) growth orientation and the lattice constants were calculated to be \(a = 6.367 ~\text{Å}~\) and \(c = 15.833 ~\text{Å}\). Figure 2b shows the Raman scattering spectrum of this CBTS film measured using a red laser of \(\lambda_{exc} = 632.8 ~\text{nm}\). Because the excitation laser wavelength is close to the bandgap of CBTS, near-resonant scattering occurs with resultant enhancement of Raman scattering efficiency and cross sections. Thus, intense vibrational bands can be observed under this condition. The irreducible representation of trigonal CBTS with a \(P3_1\) symmetry [point group \(C_3 (3)\) \((\Gamma_{optic} = 23 \Delta + 23 \Theta + 23 \Gamma)\) gives rise to the theoretical prediction of 69 optical modes (regardless of TO/LO splitting); as the structure is not centrosymmetric, all the optical modes are simultaneously Raman and IR active.\(^{[22]}\)

As shown in Figure 2b, CBTS shows 20 visible vibrational peaks with three dominant peaks at 189.9, 254.7, and 344.7 cm\(^{-1}\). These dominant bands can be regarded as totally symmetric vibrations which involve the motion of sulfur atoms alone and thus belong to “A” symmetries.\(^{[23]}\) Figure 2c shows the optical transmission spectrum of this CBTS film grown on the FTO substrate measured by ultraviolet-visible (UV-vis) spectroscopy. The CBTS film exhibits optical uniformity with interference extrema. The low transmittance (<10%) in the IR spectral region suggests that the FTO substrate remains suitably conductive after sulfurization. The linear fit of a direct bandgap plot yields the fundamental bandgap of CBTS at 2.046 eV for the lowest energy direct transition (red line in the inset of Figure 2c). Figure 2d shows the photoluminescence (PL) spectrum of this CBTS film deposited on the FTO substrate at 30 K. Spectral PL shows a maximum at 1.99 eV with an asymmetric linewidth along with a shoulder peak at 2.07 eV with a 10 meV linewidth. The 1.99 eV emission suggests that the dominant defects in CBTS result in shallow energy levels, which may primarily originate from the copper vacancies. The 2.07 eV emission with a small linewidth is characteristic with a near-band-edge exciton transition. The measured time-resolved PL (TRPL) recorded at 1.99 eV reveals a carrier lifetime of ~11 ns from the red curve fit to Equation (S1) (Supporting Information).\(^{[24]}\)

A 200 nm thick CBTS film was deposited on a Si wafer substrate for spectroscopic ellipsometry (SE) measurement. This film was characterized by XRD and Raman spectroscopy, showing a pure trigonal phase (Figure S2, Supporting Information). SE measurements were performed over the spectral range from 225 nm to 1800 nm (0.7–5.5 eV) at angles of incidence of 55\(^{\circ}\), 60\(^{\circ}\), and 65\(^{\circ}\) (Figure S3a, Supporting Information). The SE measurements at multiple angles enable surface roughness correction for determination of accurate dielectric functions. Surface roughness was modelled using the Bruggeman effective medium approximation and for different samples was adequately represented by a layer of thickness in the range of 3–5 nm composed of a 0.5/0.5 vol. fraction mixture of underlying CBTS and void (Figure S3a, Supporting Information).\(^{[25]}\) SE-derived complex dielectric function and optical absorption coefficient spectrum are shown in panels (a) and (b) of Figure 3, where dark solid lines are the best parametric fits based on a model of a sum of critical point (CP) and background modified Tauc–Lorentz oscillators.
as expressed by Equation (S2) (Supporting Information), with the fitted parameters being given in Table S2 (Supporting Information). The imaginary part \( \varepsilon_2 \) suggests an absorption onset at \( \approx 2.04 \) eV, consistent with the transmittance spectra (Figure 2c). The relative dielectric constant of CBTS \( \varepsilon_r \approx 5.4 \) was obtained approximately by fitting the data for the real part \( \varepsilon_1 \) over the near-IR photon energy range applying a first-order Sellmeier equation. \([26]\) The result is consistent with the parametric high frequency dielectric constant \( \varepsilon_\infty \approx 5.3 \). As shown in Figure 3b, CBTS exhibits a strong absorption coefficient, \( \alpha > 10^4 \text{ cm}^{-1} \) for the range of photon energies \( E > 2 \) eV. A plot of \( (\alpha E)^2 \) versus \( E \) based on SE-derived \( \alpha \) in Figure 3b inset reveals the bandgap of CBTS at \( E_g \approx 2.043 \) eV, in a good agreement with the transmission results in Figure 2c. The CP analysis from the second derivatives of complex dielectric functions (Figure S3b, Supporting Information) yields a bandgap CP of \( E_0 = 2.074 \) eV with a broadening parameter of \( \Gamma_0 = 0.094 \) eV and seven other CPs above the bandgap at room temperature (Table S2, Supporting Information).\([27]\) Temperature-dependent SE measurements shown in panels (c) and (d) of Figure 3 reveal a characteristic redshift of the bandgap CP energy \( E_0 \) and an increase in CP broadening parameter \( \Gamma_0 \) with increasing temperature. As shown in Figure 3d, \( E_0 \) and \( \Gamma_0 \) vary linearly within the studied temperature range. The best linear fit leads to a temperature narrowing coefficient of \( -3.7 \times 10^{-4} \text{ eV K}^{-1} \) for CBTS bandgap. This result may enable precise measurement of the temperature during ongoing in situ deposition of CBTS over the temperature range studied.

CdS-based buffer layers were prepared by reactively sputtering a CdS target in the mixed O\(_2\)/Ar environment at ambient temperatures, whereby the O\(_2\) contents (0%, 1%, 3%, 5%) were controlled by the flow ratio of O\(_2\)/Ar. Figure S3 (Supporting Information) shows the XRD patterns of these buffer layers deposited on soda lime glass substrates. CdS-based buffers sputtered using 0% and 1% O\(_2\) exhibit multiple XRD peaks corresponding well to wurtzite CdS, suggesting that they are well crystalline; while, there is no specific XRD peaks observed in the CdS:O buffers sputtered using 3% and 5% O\(_2\), suggesting the nanocrystalline or near amorphous crystalline structure. To identify the exact chemical component in our CdS:O buffers, X-ray photoelectron spectroscopy (XPS) measurements were conducted. XPS survey spectra in Figure S4a (Supporting Information) suggests that introducing O\(_2\) in the sputtering environment results in a great density of oxygen being incorporated into the CdS:O buffers, which is evidenced by the intense O 1s peak. A detailed measurement of the O 1s region (Figure S4b, Supporting Information) indicates that no significant Cd(OH)\(_2\) and CdO\(_x\) species is present in CdS:O buffers.\([18,19,28]\) A detailed measurement of the S 2p region (Figure S4c, Supporting Information) indicates the presence of three sulfur species, namely...
S²⁻, SO₄²⁻, and SO₃²⁻,[17] suggesting that our sputtered CdS:O buffers consist of three components: CdS, CdSO₄, and CdSO₃. The component phase fractions can be further quantified by area percentages of the S 2p peaks from these three sulfur species. We find that the CdS:O buffer sputtered using 3% O₂ is comprised of 54.65% CdS, 26.41% CdSO₄, and 18.94% CdSO₃, and that the CdS:O buffer sputtered using 5% O₂ is comprised of 15.90% CdS, 72.13% CdSO₄, and 11.97% CdSO₃. This finding suggests that with increasing oxygenation, CdSO₄ is the preferred species in CdS:O buffers at the expense of CdS, whereas CdSO₃ content remains nearly unchanged.[17,19]

Although CdS:O exhibits the multiphase feature, there is only one apparent absorption edge observed in the optical transmission spectra (Figure S5a, Supporting Information). Hence, CdS:O bandgaps can be estimated at the vicinity of absorption edge based on the relation (αE)² versus E. Figure S5b (Supporting Information) shows that the plotted bandgap value increases from 2.42 eV for CdS to 3.70 eV for CdS:O sputtered using 5% O₂, leading to the film colour variance from yellow to transparent (Figure S5c, Supporting Information).

The flat band potential technique [i.e. Mott–Schottky (MS) plot] is a simple and low-cost method to determine the band positions and the carrier density of a photoelectrode material, which is widely used in photoelectrochemistry analysis.[29] Herein, we employed this technique to evaluate CdS:O and CBTS. The n-type natures of CdS:O buffers are evidenced by the positive slopes of the measured MS plots shown in panels (a) and (b) of Figure S6 (Supporting Information). The linear-fit results of MS plots in Table S2 (Supporting Information) indicate that the CBM of CdS:O upshifts as oxygenation increases, while the carrier density decreases from 2 × 10¹⁸ to 8 × 10¹⁶ cm⁻³, consistent with the predications in the literature.[13] The p-type

---

**Figure 3.** a) Real (ε₁) and imaginary (ε₂) parts of the dielectric function with a best parametric fit at room temperature, b) dielectric function derived absorption coefficient (α) and bandgap plot at room temperature, c) temperature-dependent real (ε₁) and imaginary (ε₂) parts of the dielectric function and their best parametric fits, d) temperature-dependent parametric bandgap critical point energies (E₀) and bandgap critical point broadening parameters (Γ₀) of a CBTS film grown on a Si wafer measured by spectroscopic ellipsometry.
conductivity of CBTS is confirmed by the negative slope of the measured MS plot shown in Figure S6c (Supporting Information). The carrier density of CBTS was determined to be $0.5 \times 10^{16}$ cm$^{-3}$.

To create p–n junctions, CdS-based buffer layers were deposited on CBTS absorbers by reactively sputtering as described above. Figure 4 shows the tilted SEM images of the cross sections of CBTS films coated with sputtered CdS-based buffer layers reactively sputtered in the mixed O$_2$/Ar environment with a) 0%, b) 1%, c) 3%, and d) 5% O$_2$ at ambient temperatures, e) 1D band alignment sketches of CBTS/CdS, CBTS/CdS:O, and CBTS/CdSO$_3$,$_4$, f) schematic representation of contact information of CdS:O buffers with CBTS absorbers. Note: in panel (e), CB-conduction band, VB-valence band; red arrows and red lines in panel (e) show recombination paths (red arrows) via interface defects (red lines); black arrows in panel (f) show that the passage of electrons from the CBTS layer is only permitted via conductive CdS phases, while insulating CdSO$_3$,$_4$ phases act as good passivators of the CBTS surface.
layers using different percentages of O₂. The CdS:O layer shown in Figure 3c was sputtered for ≈4 min whereas the others were sputtered for ≈11 min. As seen, CdS:O layers show dramatically reduced grain sizes with increased oxygenation, and 5% O₂ used in the sputtering environment eventually leads to an amorphous CdS:O buffer layer, consistent with the XRD observations in Figure S4 (Supporting Information). Followed by sequential deposits of sputtered intrinsic ZnO and aluminum-doped ZnO (ZnO:Al, front contact) overlayers, CBTS solar cells were constructed with the configuration FTO/CBTS/CdS-based buffer/ZnO/ZnO:Al.

Figure 5 shows the box charts of device parameters of these CBTS solar cells measured under AM 1.5G illumination from the ZnO:Al front contact. V_{OC} is quite an important photovoltaic parameter, being most directly affected by interface and bulk recombination.\[^10\] We observe that CBTS solar cells with CdS:O buffers show remarkably higher V_{OC}'s than CdS buffered cells, and V_{OC}'s continue to increase with higher oxygenation. This observation suggests that the dominant recombination for CdS buffered CBTS solar devices takes place at the heterojunction interface where holes from CBTS recombine with electrons from CdS, largely because of the conduction band misalignment and large lattice mismatch between CBTS and CdS. As shown in Figure S6d and Table S2 (Supporting Information), CdS buffer creates a cliff-like (type II) conduction band alignment with the CBTS absorber, that is, a CBM ≈0.57 V lower than that of CBTS, usually associated with higher interface recombination rates.\[^9\] In addition, the large lattice mismatch between CBTS and CdS may cause a high density of interface defects, which can act as effective paths for carrier recombination at the heterojunction interface. As a result, interface recombination greatly limits the V_{OC}'s in CdS buffered cells, which are much less than the maximum attainable V_{OC} (=1.65 V) for the absorber with a ≈2.0 eV bandgap based on the Shockley–Queisser limit. In contrast, the high V_{OC}'s observed in CdS:O buffered cells suggest interface recombination is greatly suppressed by using CdS:O buffer. First, nanocrystalline and amorphous CdS:O grains observed in panels (c) and (d) of Figure 4 can reduce the strain at the heterojunction and lessen the need for ideal lattice-matching junctions, thus facilitating a reduction in the density of interface defects and mitigating interface recombination.\[^20\] Second, the highly resistive CdSO₄ phase in CdS:O is known to be an effective passivator for interface defects. Thus the presence of CdSO₄ at CBTS surface is able to further minimize interface recombination.\[^13,18\] Likewise, CdSO₃ may likely play a similar role in surface passivation as does CdSO₄. Besides, CdS:O shows a higher CBM than CdS, which could move the electrons in the CdS:O buffer further away from the holes in CBTS, and therefore may greatly minimize interface recombination rates.\[^13,10\] As oxygenation increases, more CdSO₄ passivators form and the CBM of CdS:O shifts to higher energy as well.\[^13,17,19\] Thus, CdS:O buffers sputtered using higher O₂ contents enable higher V_{OC}'s by reducing interface recombination. The 1D band alignment roughly sketched in Figure 4e clearly delineates this situation, namely how well CdS:O improves V_{OC}'s in the presence of interface defects as compared to the results for CdS.
The champion $V_{OC}$ of $\approx 1.1$ V was achieved by the CdS:O buffer sputtered using 5% O$_2$. But this CdS:O buffer leads to dramatically increased series resistances ($R_S$'s) as seen in Figure 5e. As has been proved by the XPS results in Figure S4 (Supporting Information), higher oxygenation will cause the formation of more CdSO$_4$ at the expense of CdS. Since CdSO$_4$ is electrically insulating, the current transport through the buffer layer will hinge on the CdS component in CdS:O. Therefore, the electron transport paths from CBTS to the front contact; conversely, it can facilitate reducing interface recombination. Figure 6a shows the $J$–$V$ curves of typical CBTS solar cells in the configuration FTO/CBTS/CdS-based buffer/ZnO/ZnO:Al, wherein CdS-based buffers were reactively sputtered in the mixed O$_2$/Ar environment with varying O$_2$ contents (5%, 3%, 1%, 0%) at ambient temperatures.

Table 1. Device parameters of FTO/CBTS/CdS-based buffer/ZnO/ZnO:Al solar cell devices, wherein CdS-based buffer layers were reactively sputtered in the mixed O$_2$/Ar environment with varying O$_2$ contents (5%, 3%, 1%, 0%) at ambient temperatures.

<table>
<thead>
<tr>
<th>CdS:O</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
<th>$R_S$ [$\Omega$ cm$^2$]</th>
<th>$R_{sh}$ [$\Omega$ cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>1.108</td>
<td>2.22</td>
<td>27.77</td>
<td>0.68</td>
<td>183.00</td>
<td>343.60</td>
</tr>
<tr>
<td>3%</td>
<td>0.906</td>
<td>4.68</td>
<td>37.80</td>
<td>1.60</td>
<td>101.50</td>
<td>658.40</td>
</tr>
<tr>
<td>1%</td>
<td>0.795</td>
<td>4.39</td>
<td>30.86</td>
<td>1.08</td>
<td>139.34</td>
<td>449.45</td>
</tr>
<tr>
<td>0%</td>
<td>0.657</td>
<td>4.15</td>
<td>46.65</td>
<td>1.28</td>
<td>43.40</td>
<td>886.65</td>
</tr>
</tbody>
</table>

Figure 6a shows the $J$–$V$ curves of typical CBTS solar cells in the configuration FTO/CBTS/CdS-based buffer/ZnO/ZnO:Al, wherein the CdS-based buffers were sputtered with varying O$_2$ contents at ambient temperatures. The corresponding device parameters are given in Table 1. The CdS:O buffer sputtered using 3% O$_2$ achieved the best CBTS solar cell with a PCE of 1.6%, a $V_{OC}$ of $\approx 0.91$ V, an FF of $\approx 0.38$, and a $J_{SC}$ of $\approx 4.7$ mA cm$^{-2}$, and shows a CBM $\approx 0.28$ V higher than that of CBTS. This slightly positive $V_{OC}$ of $\approx 0.38$ V does not block the electron transports from the CBTS to the front contact; conversely, it can facilitate reducing interface recombination. Figure 6b shows the normalized EQE curves of these CdS:O buffered devices accordingly, where it can be observed that the EQE maxima shift from $\approx 2.4$ to $\approx 3.0$ eV with the increase of O$_2$ percentages. This blueshift of EQE maxima arises from the increased bandgap values of CdS:O buffers.

In order to improve FF’s and $J_{SC}$’s and maintain high $V_{OC}$’s, reducing the thickness of CdS:O layer appears to be an effective solution, but this may increase the density of pin holes because it is challenging to deposit conformal overlayers by sputtering which are both uniform and ultrathin. As seen in Figure 6c, the sputtered CdS:O buffer with a thickness of $\approx 30$ nm does not uniformly coat CBTS film without pin holes. The presence of pin holes may cause direct contacts between ZnO and CBTS and cause severe interface recombination. In this regard, we designed a bilayer buffer which includes an ultrathin CdS:O layer sputtered using 3% O$_2$ for $\approx 2$ min plus a thicker layer of CdS sputtered in pure Ar for $\approx 5$ min. This bilayer buffer design may form a favourable band alignment with CBTS for photocurrent extraction without sacrificing $V_{OC}$’s. Panels (a) and (b) of Figure 7 show the cross-sectional SEM images of a finished CBTS solar device with the configuration FTO/CBTS/CdS:O/CdS/ZnO/ZnO:Al. The $\approx 2$ μm thick CBTS absorber layer shows an equiaxed large-grain (>1 μm) microstructure with microvoids being observed at the film rear side (Figure 7a). As shown by the magnified SEM images in Figure 7b, there is no clear interface boundary between CdS:O and CdS layers, which is preferred to circumvent the parasitic interface recombination between CdS:O and CdS.
to the device results based on the bare CdS:O buffer sputtered using 3% O₂ (Figure 5), this bilayer buffer achieves significantly improved FF’s and slightly improved $V_{OC}$’s, both of which contribute to higher PCE’s (Figure 7c).

Our best CBTS solar cell was achieved with this bilayer buffer and exhibited a PCE of 2.03%, a $V_{OC}$ of 0.933 V, a FF of 0.43, and a $J_{SC}$ of 5.08 mA cm$^{-2}$ under AM 1.5G illumination from the ZnO:Al front contact (Figure 7d). The EQE spectra measured under reverse ($−1$ V) and zero biases of this record CBTS device are shown in Figure 7e. The integrated $J_{SC}$ from the 0 V biased EQE, 5.2 mA cm$^{-2}$ (Figure S7, Supporting Information), is consistent with that from the $J$–$V$ measurement. Under a reverse bias, the depletion region extends into CBTS allowing more photogenerated carriers to be collected, resulting in an increased EQE as compared to the 0 V biased EQE. The ratio of EQE responses, in the form of ($−1$ V)/0 V, shows a gradual increase toward the longer wavelengths, indicating less collection of photocurrents at the rear side of CBTS.

The inflection point of the 0 V biased EQE spectrum yields an absorption onset of 2.05 eV for the CBTS absorber, which is consistent with the values measured from UV-vis spectroscopy (Figure 2c inset), SE (Figure 3b inset) and the first
derivatives of the normalized EQE curves in Figure 6b (Figure S8, Supporting Information). The inflection point at 2.33 eV very likely derives from a higher energy CP \( (E_F) \) as denoted in panels (a) and (b) of Figure 3. The spatial carrier distribution of this record CBTS solar cell was characterized by capacitance–voltage (C–V) derived profiles of \( N_{CV} \) versus \( \langle x \rangle \) as shown in Figure 7f, where \( \langle x \rangle \) is the profiling distance from the junction. The \( \langle x \rangle \) value of 751–774 nm at zero bias corresponds to the depletion region width of the CBTS solar cell, which is much less than the CBTS film thickness. As reverse biases were applied, the depletion region width was extended into the CBTS bulk region, allowing the carrier density of CBTS away from the junction region to be tested. \( N_{CV} \) profiles indicate that CBTS has a carrier density of 0.3–1.2 \( \times \) \( 10^{16} \) cm\(^{-3}\), consistent with the values derived from the MS plot in Table S2 (Supporting Information). A rapid increase of \( N_{CV} \) at positive biases exceeding 0.7 V corresponds to the high carrier density in CdS. \( N_{CV} \) profiles measured at 300 kHz and 10 kHz additionally show a small profiling distance shift of \( \Delta \langle x \rangle = 23 \) nm, suggesting no robust electrical barrier (either second diode or nonohmic contact) present in the device.[12]

3. Conclusions

In this work, earth-abundant CBTS thin films were fabricated by postsulfurization of cosputtered sulfide precursors. Characterization measurements based on UV–vis spectroscopy, SE, Raman scattering, and C–V profiles were conducted to acquire the fundamental physical parameters of CBTS, including optical absorption coefficient (\( \geq 10^4 \) cm\(^{-1}\)), band gap (2.04–2.07 eV), complex dielectric function, CPs for optical transitions, lattice vibrational modes, and carrier density (\( \simeq 10^{16} \) cm\(^{-3}\)). Temperature-dependent SE measurements additionally reveal that CBTS has a bandgap narrowing coefficient of \( \approx -4 \times 10^{-4} \) eV K\(^{-1}\) with increasing temperature. PL spectroscopy measurements suggest that the dominant defects in CBTS produce shallow energy levels.

CdS:O buffer layers were deposited on CBTS absorbers to create p–n junctions by reactively sputtering a CdS target in the mixed O\(_2\)/Ar environment. XPS measurements suggest that CdS:O is a mixture of CdS, CdSO\(_4\), and CdSO\(_3\). The \( V_{OC} \)'s of CBTS solar cells were enhanced through increased oxygenation in CdS:O buffers. A sputtered CdS:O buffer layer using 5% O\(_2\) yielded the best \( V_{OC} \) of \( \approx 1.1 \) V among our CBTS solar cells; but this buffer greatly degraded the other device parameters as evidenced by large \( R_S \)'s, poor FF's, and small \( J_{SC} \)'s. Thus, the oxygen content in the sputtering environment and the thickness of CdS:O layer must be chosen with caution. In order to maintain high \( V_{OC} \)'s without sacrificing the other device parameters, a bilayered buffer was applied to the CBTS solar cells, which includes an ultrathin layer of sputtered CdS:O using 3% O\(_2\) plus a thicker layer of sputtered CdS using pure Ar. This buffer design yielded our best-performing CBTS solar cell with a PCE of 2.03%, a \( V_{OC} \) of 0.93 V, an FF of 0.43, and a \( J_{SC} \) of 5.08 mA cm\(^{-2}\).

This work demonstrates that CBTS is a promising earth-abundant material suitable as a top-cell absorber in tandem solar devices and also suggests that the optimization of interfacial contact between CBTS and buffer layers is critical to \( V_{OC} \) enhancement. This work additionally opens a new area of wide bandgap photovoltaic materials within the trigonal and orthorhombic system of (Cu, Ag, Au)\(_x\)(Sr, Ba, Eu)\(_y\)(Ge, Sn)\(_z\)\((S, Se)\)_4\(^{1,5,13}\) wherein none of the system members has gained much attention before.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgment

This work was supported by the National Science Foundation under contract no. CHE-1230246 and DMR-1534686, and Ohio Research Scholar Program. Weiwei Meng is thanked for his continuous supports in calculating the band structures of new quaternary chalcogenides.

Received: August 17, 2016
 Revised: October 11, 2016
Published online:

---


