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Riley E. Brandt, Matthew Young, Helen Hejin Park, Arrelaine Dameron, Danny Chua, Yun Seog Lee, Glenn Teeter, Roy G. Gordon, and Tonio Buonassisi

Abstract: The development of cuprous oxide (Cu$_2$O) photovoltaics (PVs) is limited by low device open-circuit voltages. A strong contributing factor to this underperformance is the conduction-band offset between Cu$_2$O and its $n$-type heterojunction partner or electron-selective contact. In the present work, a broad range of possible $n$-type materials is surveyed, including ZnO, ZnS, Zn(O,S), (Mg,Zn)O, TiO$_2$, CdS, and Ga$_2$O$_3$. Band offsets are determined through X-ray photoelectron spectroscopy and optical bandgap measurements. A majority of these materials is identified as having a negative conduction-band offset with respect to Cu$_2$O; the detrimental impact of this on open-circuit voltage ($V_{OC}$) is evaluated through 1-D device simulation. These results suggest that doping density of the $n$-type material is important as well, and that a poorly optimized heterojunction can easily mask changes in bulk minority carrier lifetime. Promising heterojunction candidates identified here include Zn(O,S) with [S]/[Zn] ratios $>$70%, and Ga$_2$O$_3$, which both demonstrate slightly positive conduction-band offsets and high $V_{OC}$ potential. This experimental protocol and modeling may be generalized to evaluate the efficiency potential of candidate heterojunction partners for other PV absorbers, and the materials identified herein may be promising for other absorbers with low electron affinities. © 2014 AIP Publishing LLC.

Cuprous oxide (Cu$_2$O) is a promising Earth-abundant photovoltaic (PV) absorber, however, its technological relevance is limited by low PV conversion efficiencies. In particular, historical cells demonstrate low open-circuit voltages ($V_{OC}$) relative to their Shockley-Queisser entitlement of 1.6 V. While low minority-carrier lifetime contributes to underperforming $V_{OC}$, recent work suggests that a dominant $V_{OC}$ loss mechanism is the conduction-band alignment (offset) between Cu$_2$O and its heterojunction partner, herein referred to as the electron-selective contact (ESC). Engineering this offset has led to open-circuit voltages as high as 1.2 V, thus, we identify control, measurement, and modeling of the ESC conduction-band alignment as a critical area of research for Cu$_2$O. This method for screening the $V_{OC}$ potential of candidate ESCs generalizes to other $p$-type absorber materials as well.

The search for more optimal ESCs is especially difficult due to the low electron affinity of Cu$_2$O ($\chi = 3.2$ eV); materials with such a low electron affinity are often challenging to dope due to self-compensation by intrinsic defects. Several authors have measured negative, or “cliff”-type conduction-band offsets between Cu$_2$O and other materials to explain the cause of low $V_{OC}$, including ZnO ($-1.0 \rightarrow -1.8$ eV$^4$, $2.4$, $8$, $9$, In$_2$O$_3$ ($-0.83$ eV$^{10}$), TiO$_2$ ($-0.74$ eV$^{11}$), GaN ($-0.23$ eV$^{12}$), as well as ZnS and ZnSe. In the present study, we specifically measure $n$-type materials deposited by atomic layer deposition (ALD) or pulsed laser deposition on electrochemically deposited Cu$_2$O terminated with a stoichiometric Cu$_2$O surface. The ESC materials explored include ZnO, TiO$_2$, Ga$_2$O$_3$, CdS, and (Mg,Zn)O:Ga.

Electronic band offsets are sensitive to grain orientation, surface atomic termination, adsorbed extrinsic species, chemical reactions, and interdiffusion. Prior work suggests that the offset on Cu$_2$O is influenced by the presence of monolayers of CuO at the surface, which may explain the variation in literature reports of band offsets. To control for these effects, all Cu$_2$O surfaces here are (111) terminated and show only the $+1$ oxidation state of copper as measured by X-ray photoelectron and Auger electron spectroscopy.

Cu$_2$O is deposited by constant-current two-electrode electrochemical deposition from a basic solution of copper sulfate, lactic acid, and sodium hydroxide. The deposition parameters are described in prior work. A bath pH of 12.5 leads to the highly preferential (111) surface orientation. The film is rinsed in DI water (18.6 MQ), and stored and transferred in a N$_2$ ambient glovebox to prevent surface oxidation to CuO. Unless stated otherwise, all depositions onto the Cu$_2$O are performed with a substrate temperature of 120°C.

ZnO$_x$S$_y$ and Ga$_2$O$_3$ overlayers are deposited by ALD with a custom tube furnace ALD reactor. Diethylzinc$^{15}$ and bis(µ-dimethylamino)tetrakis(dimethylamino)digallium$^5$ are used for the Zn and Ga precursors, respectively; deionized H$_2$O and 4% H$_2$S in N$_2$ are used for the oxide and sulfide anion precursors.

ZnO, CdS, and TiO$_2$ overlayers are deposited by ALD using a Beneq TFS200 ALD reactor. The cation precursors used are diethylzinc, dimethylcadmium, and titanium isoproxide, respectively, while the anion precursors are the...
same as above. Deposition temperatures were again 120°C except for TiO₂ deposited at 150°C.

A gallium-doped magnesium zinc oxide alloy, (Mg,Zn)O:Ga, is deposited by pulsed laser deposition using two fixed-composition ceramic targets with 21% Mg or 6% Mg and 1% Ga; the deposition tool is described elsewhere. The depositions were conducted at a chamber pressure of 9 mTorr, with a 99% Ar and 1% O₂ gas environment.

The valence- and conduction-band offsets are measured through a combination of X-ray photoelectron spectroscopy (XPS), UV-visible spectrophotometry, and spectroscopic ellipsometry. XPS is performed with a Kratos AXIS Nova tool, with a photon energy of 1486.6 eV. Samples experienced <10 min of ambient air exposure during mounting, then were pumped down to pressures <10⁻⁸ mTorr for measurements. The binding energy scale is calibrated in each run by a linear least squares fitting of reference core levels of Cu 2p, Ag 3d, Mo 3d, and Au 4f, as well as Fermi levels of all four metals.

The valence band offset (ΔEV) is determined by the Kraut method through XPS, using core-level offsets from heterojunction samples

\[
ΔE_V = (E^c_{Cu_2O} - E^n_V) - (E^c_{Cu_2O} - E^n_{core}) - (E^c_{Cu_2O} - E^n_{ZnS}) + (E^n_{core} - E^n_V),
\]

where E_V is the valence band maximum of Cu₂O or the n-type material and E_{core} is a specific core level for the Cu₂O or n-type material. Three samples are requisite—two bulk, homogeneous films to determine the core level to valence band offsets, and one heterojunction film with a thin overlayer on Cu₂O to determine the core level offsets. ALD ensures conformal overlayer coverage even at these thicknesses. The extraction of all three terms in Eq. (1) is demonstrated in Fig. 1 for ZnS on Cu₂O, where E_F is the Fermi energy, E_C is the conduction-band energy, and E_{core} represents the respective bandgaps.

To extract the conduction-band offset, ΔEC, we add the difference in bandgap of the Cu₂O and ESC materials to ΔEV. E_Q is determined by fitting the absorption coefficient, measured through UV-visible spectrophotometry or spectroscopic ellipsometry. This necessarily assumes that the optical bandgap is identical to the fundamental bandgap (no Moss-Burstein shift), and that the surface bandgap is the same as the bulk bandgap.

The n-type materials in this study are amorphous with the exception of (Mg,Zn)O, pure ZnO, CdS, and pure ZnS as verified by X-ray diffraction (XRD). For amorphous materials, the band edge is fit by the Tau method, extrapolating the linear region of E_{photon} vs. (zhv)^½, and for crystalline materials using the plot of E_{photon} vs. (zhv)^2 instead. The bandgap of Ga₂O₃ was determined previously to be 5.18 eV.⁵

For each material evaluated, the valence band offset is determined using the core level offset for an overlayer <2 nm thick. Given a carrier concentration in the overlayer of less than 1 x 10¹⁸ cm⁻³, this results in a maximum electric field at the heterojunction of less than 5 x 10⁴ V/cm. This corresponds to a shift in the binding energies of <0.01 eV over a 2 nm distance; thus, we assume that the effect of band bending is minimal over the typical XPS information depth.

FIG. 1. Routine for ΔEV extraction using 2 nm ZnS overlayers, with three samples; (a) band diagram of heterojunction with core-level to valence bands of separate bulk samples, and core-level offset; (b) valence band edges of pure, bulk samples; (c) Cu 2p core levels of pure bulk Cu₂O and with a thin overlayer; (d) Zn 2p core levels of pure bulk ZnS and in a thin overlayer sample.

The results of the core level to valence band and core level to Cu 2p 3/2 core level offsets are catalogued in Table I for each n-type material.

A 95% confidence interval for all valence-band offset measurements is determined to be ±0.10 eV by measuring eight identical Cu₂O samples. Error bars for the bandgap are determined from selecting different fitting regions and computing the standard error of the least-squares fit line. The error bars in the conduction-band offsets are assumed to be the sum of the bandgap and valence band offset errors. All of the offsets measured here are plotted in Fig. 2.

To determine an optimal conduction-band offset, we simulate the effect of ΔEC on Voc and solar cell efficiency. The Voc is determined by the hole and electron electrochemical potential difference, or quasi-Fermi level separation in the material. This separation may be limited by bulk recombination, which reduces the concentration of free photocreated carriers, or limited by the electrochemical potential of electrons in the n-type ESC. At the heterojunction interface, the recombination current, J_{0,RF}, may be modeled as

\[
J_{0,RF} = S_h N_V e^{-\frac{q\phi_b}{kT}},
\]

where S_h is the hole surface recombination velocity (SRV) at the heterojunction and is proportional to interface defect density and capture cross-section, N_V is the valence band density.
TABLE I. Extracted parameters for each n-type material from XPS and optical bandgap measurements, and the resulting band offsets including error estimates for bandgap $E_{\text{G}}$, $\Delta E_V$, and $\Delta E_C$. Cu$_2$O (Ref. 20) and Ga$_2$O$_3$ (Ref. 5) bandgaps taken from prior work.

<table>
<thead>
<tr>
<th>Material</th>
<th>Core level</th>
<th>$E_{\text{core}} - E_V$ (eV)</th>
<th>$E_{\text{core}} - E_{\text{Cu2p}}$ (eV)</th>
<th>$E_V - E_F$ (eV)</th>
<th>$E_G$ (eV)</th>
<th>$\Delta E_V$ (eV)</th>
<th>$\Delta E_C$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O</td>
<td>Cu 2p 3/2</td>
<td>931.97</td>
<td>...</td>
<td>0.35</td>
<td>2.09</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn 2p 3/2</td>
<td>1018.76</td>
<td>89.30</td>
<td>3.42</td>
<td>3.26 ± 0.01</td>
<td>-2.51 ± 0.10</td>
<td>-1.34 ± 0.11</td>
</tr>
<tr>
<td>Mg$<em>{0.06}$Zn$</em>{0.93}$O</td>
<td>Zn 2p 3/2</td>
<td>1018.75</td>
<td>89.55</td>
<td>3.72</td>
<td>3.71 ± 0.05</td>
<td>-2.77 ± 0.10</td>
<td>-1.15 ± 0.15</td>
</tr>
<tr>
<td>Mg$<em>{0.21}$Zn$</em>{0.78}$O</td>
<td>Zn 2p 3/2</td>
<td>1018.62</td>
<td>89.47</td>
<td>4.03</td>
<td>3.94 ± 0.02</td>
<td>-2.82 ± 0.10</td>
<td>-0.97 ± 0.12</td>
</tr>
<tr>
<td>ZnO$<em>{0.42}$Si$</em>{0.58}$</td>
<td>Zn 2p 3/2</td>
<td>1019.12</td>
<td>89.14</td>
<td>2.98</td>
<td>3.02 ± 0.02</td>
<td>-1.99 ± 0.10</td>
<td>-1.06 ± 0.12</td>
</tr>
<tr>
<td>ZnO$<em>{0.82}$Si$</em>{0.18}$</td>
<td>Zn 2p 3/2</td>
<td>1019.87</td>
<td>89.25</td>
<td>2.28</td>
<td>2.60 ± 0.05</td>
<td>-1.35 ± 0.10</td>
<td>-0.84 ± 0.15</td>
</tr>
<tr>
<td>ZnO$<em>{0.64}$Si$</em>{0.36}$</td>
<td>Zn 2p 3/2</td>
<td>1020.08</td>
<td>89.27</td>
<td>2.20</td>
<td>2.76 ± 0.04</td>
<td>-1.16 ± 0.10</td>
<td>-0.49 ± 0.14</td>
</tr>
<tr>
<td>ZnO$<em>{0.50}$Si$</em>{0.50}$</td>
<td>Zn 2p 3/2</td>
<td>1020.20</td>
<td>89.22</td>
<td>2.38</td>
<td>2.96 ± 0.04</td>
<td>-0.99 ± 0.10</td>
<td>-0.12 ± 0.14</td>
</tr>
<tr>
<td>ZnO$<em>{0.42}$Si$</em>{0.58}$</td>
<td>Zn 2p 3/2</td>
<td>1020.25</td>
<td>89.18</td>
<td>2.27</td>
<td>2.93 ± 0.02</td>
<td>-0.90 ± 0.10</td>
<td>-0.06 ± 0.12</td>
</tr>
<tr>
<td>ZnS</td>
<td>Zn 2p 3/2</td>
<td>1020.20</td>
<td>89.18</td>
<td>2.27</td>
<td>3.67 ± 0.01</td>
<td>-0.95 ± 0.10</td>
<td>0.63 ± 0.11</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Ti 2p 3/2</td>
<td>455.63</td>
<td>-473.78</td>
<td>3.72</td>
<td>3.44 ± 0.01</td>
<td>-2.56 ± 0.10</td>
<td>-1.21 ± 0.11</td>
</tr>
<tr>
<td>CdS</td>
<td>Cd 3d 5/2</td>
<td>403.48</td>
<td>-527.52</td>
<td>2.64</td>
<td>2.38 ± 0.02</td>
<td>-0.97 ± 0.10</td>
<td>-0.68 ± 0.12</td>
</tr>
<tr>
<td>Ga$_2$O$_3$</td>
<td>Ga 2p 3/2</td>
<td>1114.91</td>
<td>185.65</td>
<td>4.21</td>
<td>5.18 ± 0.02</td>
<td>-2.71 ± 0.10</td>
<td>0.38 ± 0.12</td>
</tr>
</tbody>
</table>

FIG. 2. Band energies (in flat-band condition) of n-type materials with respect to Cu$_2$O and their respective error bars. All energies are referenced to the valence band of Cu$_2$O.

of states in Cu$_2$O, $\phi_{\text{B}}$ is the potential barrier for holes at the heterojunction (see Fig. 3(a)), $q$ is the charge of an electron, and $k_B T$ is the product of the Boltzmann constant and temperature. If this recombination current is the dominant recombination mechanism, the $V_{\text{OC}}$ is limited to a maximum of $\phi_{\text{B}}$, which is determined by the conduction-band offset and donor/acceptor density $N_D/N_A$ ratio between the ESC and Cu$_2$O. Thus, we would expect the $V_{\text{OC}}$ to improve with increasing donor density in the buffer ($N_D$), a less cliff-like conduction-band offset, and decreasing SRV.

We quantify this with a SCAPS-1D device model of a heterojunction thin-film Cu$_2$O device. Here, the Cu$_2$O is assumed to have a 1 cm$^2$ V$^{-1}$ s$^{-1}$ minority carrier mobility, typical of electrochemically deposited Cu$_2$O. The Cu$_2$O and n-type partners are modeled with bandgaps of 2.09 eV (Ref. 20) and 3.3 eV, as well as carrier concentrations of $10^{15}$ cm$^{-3}$ and $10^{16}$–$10^{19}$ cm$^{-3}$, respectively. Changing the concentration of neutral, mid-gap interface defects influences the interface recombination velocity, while changing the concentration of neutral mid-gap bulk defects influences the bulk lifetime. As expected, the $V_{\text{OC}}$ decreases with increasing SRV, and drops linearly with decreasing conduction-band offset and logarithmically with decreasing ESC donor density (Fig. 3(c)) for cliff-type offsets. A thousand-fold increase in bulk lifetime results in minimal change in $V_{\text{OC}}$ over this region.

For near-zero $\Delta E_C$, the $V_{\text{OC}}$ becomes bulk-recombination dominated instead, and is determined by bulk lifetime alone, making it insensitive to changes in $\Delta E_C$ and SRV (Fig. 3(b)), as well as ESC donor density (Fig. 3(c)). The transition between these bulk-recombination and interface-recombination limits occurs at different offsets depending upon the SRV and ESC doping density. In the extreme case of a defect-free interface (low SRV) and low-lifetime bulk material, a slight cliff can moderately improve the $V_{\text{OC}}$ by providing a barrier for electrons in the ESC from diffusing back into the low-lifetime bulk Cu$_2$O and recombining with holes. This effect disappears at higher SRVs.

The importance of simultaneous optimization of the band alignment, reduction in defect density, and maximization of ESC doping density is exemplified by the case of silicon heterojunction with intrinsic thin layer (HIT) cells, which enables these heterojunction solar cells to exhibit higher $V_{\text{OC}}$ than homojunction cells by reducing emitter and interface recombination.

Based on these simulation results, for many conventional n-type electron-selective contacts or buffer layers, the...
band alignment on Cu$_2$O is not favorable for fabricating a high-quality heterojunction. This is demonstrated by the large conduction-band cliff measured for ZnO, TiO$_2$, and CdS.

However, alloying in the ZnO system demonstrates the potential for improving conduction-band alignment, especially when S assumes fractional occupancy on the anion site. Significant bandgap bowing necessitates going to high sulfur contents to achieve good alignment. While pure ZnS demonstrates a prohibitively large spike, intermediate compositions with a [S]/[Zn] ratio >70% show near-ideal alignment (note here that the ALD Zn(O,S) has a total anion/cation ratio greater than one due to extra hydroxide and oxide incorporation). Attempts to increase the ZnO conduction band via cation substitution are only marginally successful; this explains why alloying with Mg or Sn on the Zn site has been insufficient to make a high-performance heterojunction.\(^\text{4,3}\)

Another promising material is Ga$_2$O$_3$, which offers near ideal electronic alignment. This alignment has led to the record-high open circuit voltages in thermally oxidized (0.8 V)\(^\text{26}\) and electrochemically deposited (1.2 V)\(^\text{5}\) Cu$_2$O cells. The offset measured in the present study represents an increase over the previous measurement of $-0.18 \pm 0.16$ eV,\(^\text{5}\) which is likely due to differences in surface preparation or deposition conditions. This highlights the necessity of direct measurements under device-relevant conditions.

To address interface defect density and SRV, we limit the formation of detrimental surface phases during storage and processing. All bare Cu$_2$O surfaces show no evidence of Cu$_2$O phase, which has been identified as a detrimental defect at Cu$_2$O heterojunctions.\(^\text{4,27}\) For sulfides used here, we note that exposure of a clean Cu$_2$O surface to the H$_2$S sulfur precursor, under typical ALD conditions, resulted in the formation of Cu-S bonds at the surface as evidenced by the presence of S core peaks in XPS. However, it is unclear whether Cu-S bonds form at the interface during sulfide deposition. This is because it is difficult to distinguish between Cu$_2$S and Cu$_2$O at a buried interface using XPS, given their nearly identical core electron binding energies.

In summary, one promising strategy to improve conduction-band alignment with Cu$_2$O’s low electron affinity involves creating ternary alloys from conventional ESC materials. Alloying on the anion site with larger isovalent elements pushes the valence-band and conduction-band orbitals up to higher energies. This is demonstrated here with Zn(O,S), which shows an ideal conduction-band offset for sulfur contents >70%. Similar improvements alloying with Mg on the cation site are limited by the poor miscibility of (Mg$_x$Zn$_{1-x}$)O at higher Mg content. The success of this ternary approach also suggests that intermediate compositions of (Zn$_x$Cd$_{1-x}$)S would also have optimal alignment.

A second approach is to seek unconventional $n$-type buffer layers that may have reduced conductivity, but an innately lower electron affinity. Ga$_2$O$_3$ is demonstrated here as a promising candidate, which explains its role in the highest performing literature devices to date. However, the simulation results suggest that higher carrier concentration is necessary for high-performing devices, thus, extrinsic doping of Ga$_2$O$_3$ (e.g., Sn, Ge, F), and Zn(O,S) (e.g., Al, Ga, F) are high-priority areas of research.

Other emerging PV absorber materials including Sn$_2$S or Zn$_3$P$_2$ exhibit similarly low electron affinities as Cu$_2$O. The present work points to the challenges in pairing these absorbers with conventional $n$-type buffer layers. However, it also points to the value of developing ternary, tunable buffer layers, and unconventional materials that may greatly expand the range of commercially viable PV materials in the future.

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R.E.B. designed the experiment, fabricated Cu$_2$O and PLD samples, and wrote the paper; M.Y. took XPS measurements; R.E.B., M.Y., and G.T. analyzed the data; H.H.P., A.D., and D.C. deposited ALD films and took optical data; Y.S.L., R.G.G., and T.B. advised in experimental planning, reviewed data analysis, and assisted in manuscript preparation.

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19. See supplementary material at http://dx.doi.org/10.1063/1.4905180 for determination of bandgaps from Tauc plots, and quantification of error bars.