A Comparative Study of Defect States in Evaporated and Selenized CIGS(S) Solar Cells

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Current-voltage, admittance spectroscopy, and drive-level capacitance profiling measurements were taken on Cu(In1–xGax)Se2 and Cu(In1–xGax)(Se1–ySly)2 solar cell devices. The devices were made using two different types of absorbers. One set of absorbers was deposited via physical vapor deposition, while the other set of absorbers was made by selenization of metal precursors. Additionally, each type of absorber was completed with one of two different types of buffer treatments: a CdS layer or a cadmium partial electrolyte surface modification. The devices with the evaporated absorbers had larger values of Voc, higher carrier densities, lower densities of trapping defects, and likely shallower gap states. Results were qualitatively similar for the CdS and partial electrolyte buffers. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS: CIGS(S); solar cells; defects; carrier density; AS; DLCP; polycrystalline; Cd PE

INTRODUCTION

Thin-film solar cells made with two different processes for the deposition of Cu(In1–xGax)Se2 (CIGS) or Cu(In1–xGax)(Se1–ySly)2 (CIGSS) absorbers were studied using current–voltage (J–V), quantum efficiency (QE), admittance spectroscopy (AS), and drive-level capacitance profiling (DLCP) measurement techniques in an attempt to correlate spatial defect profiles with solar cell performance. One set of absorbers was deposited using physical vapor deposition and the other set of absorbers was prepared by selenization of metal precursor films. The absorbers deposited by physical vapor deposition were prepared using the patented three-stage process at the National Renewable Energy Laboratory (NREL) and will be referred to as 'evaporated'.1–2 The absorbers prepared by selenization were grown at Siemens (now Shell) Solar Industries (SSI) in Camarillo, California and will be referred to as 'selenized'.3,4

Currently the highest-efficiency laboratory CIGS cells come from the three-stage evaporation process, whereas the highest-efficiency large-area CIGS(S) modules are made using selenization of the metallic elements. The motivation for making devices that differ only in their absorbers is to correlate device performance...
with quantifiable electronic state differences between the two types of devices. The evaporated absorbers are CIGS, while the selenized absorbers also contain sulfur and will be referred to as CIGSS. Some reports have suggested that incorporation of sulfur may passivate defects,\textsuperscript{5–7} but we did not find evidence for reduced defects in the sulfur-containing cells. For the results reported here, the difference in deposition processes appears to play a more significant role than the partial substitution of selenium by sulfur.

In addition to absorber differences, two types of buffer treatments were compared. The junctions in several devices of each absorber type were formed using a standard chemical bath deposition (CBD) resulting in a CdS buffer layer, while other nominally identical absorbers were treated in a sulfur-free bath to prepare a non-CdS junction. The latter process, referred to as the cadmium partial electrolyte (Cd PE), modifies the absorber surface, but does not result in a separate device layer.\textsuperscript{6,9} The original motivation was to explore Cd PE as an alternative buffer layer process to CdS deposition and thus better understand junction formation and the role of Cd in the CIGS surface layer.\textsuperscript{8} However, Cd PE devices are also of interest because their high bandgap window layer improves the current of the device and because the Cd PE process produces less waste than the typical CBD–CdS process. All devices were then completed with depositions of an $i$-ZnO layer, an $n$-ZnO layer, and Ni/Al grids for contact. The resulting sample set consisted of the four different types of devices from combinations of the two types of absorbers and the two junction preparation techniques.

**RESULTS**

Prior to temperature-dependent capacitance measurements including AS and DLCP, comparative $J$–$V$ and QE measurements were made, primarily at room temperature. The illuminated $J$–$V$ curves from representative cells selected from each of the four fabrication modes are shown in Figure 1(a), and the corresponding QE curves are shown in Figure 1(b). The cell parameters deduced from the $J$–$V$ measurements, as well as the bandgaps deduced from the long-wavelength cutoff of the QE curves, are listed in Table I.

For devices made with a common buffer layer, CdS or Cd PE, the evaporated absorbers had consistently higher $V_{OC}$ values and consistently higher bandgaps than the selenized cells. The bandgap difference between evaporated and selenized devices was about 70 meV. Even after adjustment for this difference, the evaporated devices with each buffer type had larger $V_{OC}$ values than the selenized devices made with the same buffer. As shown in both Figure 1 and Table I, the evaporated devices also had a higher fill factor (FF). This is due in part to a slightly lower diode quality factor A, which often correlates with higher voltage. Also apparent from both Figure 1 and Table I is the larger short-circuit current density $J_{SC}$ of the Cd PE devices (triangles in the figure), primarily due to improved current collection at wavelengths less than 520 nm.

Admittance spectroscopy (AS) measurements, i.e., capacitance and conductance as a function of frequency at multiple temperatures, were taken on the four types of samples. There was no d.c. bias applied during these measurements, and the data were gathered at temperatures ranging between 100 and 300 K. The majority of the AS measurements were taken at the University of Oregon using an SRS 850 lock-in amplifier and SRS 570 current to voltage preamplifier. However, two of the samples were measured at Colorado State University using an HP 4192A LF impedance analyzer. The results from the two instruments were entirely consistent. More details on AS can be found in the literature.\textsuperscript{10–14} Representative scans of capacitance per unit area ($C/A$) versus frequency ($f$) for each of the four device types are shown in Figures 2 and 3. The AS data (Figure 2) from the evaporated cells shows very little variation as a function of frequency, while that from the selenized cells (Figure 3) shows a much larger difference between high and low frequencies. All curves had significant noise at the lowest frequencies.

A downward step in a capacitance–frequency isotherm is indicative of a transition from a frequency–temperature region where a defect responds (i.e., where it traps and releases carriers at a rate greater than the measurement frequency) to a region where the same defect is not able to respond to the applied frequency. The broader transitions seen in this work are indicative of a range of defect energies.

Defect levels can affect the solar cells in at least two ways: shallower levels can improve device performance by contributing carriers at room temperature, while deeper levels can detract from device performance by enhancing recombination. We assume a fairly simple model in which the high-frequency capacitance reflects...
the response of the free carrier density, while the low-frequency capacitance reflects the sum of the carrier plus trap densities.\textsuperscript{15} The evaporated devices in Figure 2 showed small, yet measurable, changes in capacitance with frequency, indicative of a small density of defects acting as hole traps, while the selenized devices in Figure 3 exhibited significant frequency dependence of the capacitance, indicative of a large density of hole traps. Measurements on similar devices yielded roughly the same results.

Figures 2 and 3 also show the difference between the values of the high-frequency capacitance/area (C/A) for the evaporated and selenized devices. Assuming that there is no significant charge density at the interface, and the absorbers are reasonably uniform spatially, the evaporated devices (Figure 2) indicate an approximate free carrier (hole) density in the low-10\textsuperscript{15} cm\textsuperscript{3} range, while the selenized devices have high frequency C/A values that lead to an approximate free carrier (hole) density mostly in the mid-10\textsuperscript{14} cm\textsuperscript{3} range. Thus, AS suggests that there are more free carriers, as well as fewer trapping defects in the evaporated devices. The approximate free-carrier and trapping densities are summarized in Table II.

Table I. Summary of illuminated J–V results and bandgap deduced from room temperature QE measurement. J–V measurements were taken under standard illumination (100 mW/cm\textsuperscript{2}) at room temperature. $\Delta E_g = 1.15 \text{ eV} - E_g$

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{OC}$ (V)</th>
<th>$E_g$ (eV)</th>
<th>$V_{OC} + \Delta E_g/q$ (V)</th>
<th>$J_{SC}$ (mA/cm\textsuperscript{2})</th>
<th>Fill factor (%)</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenized Cd PE</td>
<td>0.521</td>
<td>1.07</td>
<td>0.597</td>
<td>32.8</td>
<td>65.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Selenized CdS</td>
<td>0.564</td>
<td>1.08</td>
<td>0.633</td>
<td>30.7</td>
<td>68.8</td>
<td>~2</td>
</tr>
<tr>
<td>Evaporated Cd PE</td>
<td>0.615</td>
<td>1.14</td>
<td>0.622</td>
<td>31.8</td>
<td>72.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Evaporated CdS</td>
<td>0.690</td>
<td>1.15</td>
<td>0.690</td>
<td>29.7</td>
<td>78.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>
The Table II estimates use numerical analysis methods,\textsuperscript{16} assuming a defect energy distributed uniformly throughout the depletion region. Uncertainties in its energy and the value of built-in potential lead to a factor-of-two uncertainty in values for free-carrier and defect densities. Other modeling parameters such as the effective density of states, thermal emission prefactor, and width of the defect band have little effect on the Table II estimates.

Defining $f_i$ as the frequency at which the capacitance is half-way between our best estimates of the high- and low-frequency limits for each AS curve, and using the measurement temperature for each curve, we calculated an average thermal activation energy $E_a$ for the detected defects from the relationship\textsuperscript{12–14}

$$2\pi f_i/T^2 = \nu_0 \exp(-E_a/k_B T)$$

Figure 2. Admittance spectroscopy results for: (a) an evaporated, CdS device; (b) an evaporated, Cd PE device. Different symbols represent different measurement temperatures. Measurements were taken at 20 K intervals at zero applied bias.

Figure 3. Admittance spectroscopy results for: (a) a selenized, CdS device; (b) a selenized, Cd PE device. Different symbols represent different measurement temperatures. Measurements were taken at 20 K intervals at zero applied bias.
where \( \nu_0 = \sigma_p \nu_{th} N_v / T^2 \). The individual factors (hole cross section \( \sigma_p \), thermal velocity \( \nu_{th} \), and the effective density of states in the valence band \( N_v \)) are not independently determined and are not critical for these results. When there is one well-defined activation energy \( E_a \) for the defect response, one usually identifies this as the approximate energy difference between the valence band edge and the available energy state in the bandgap created by the defect. A band of defects covering a small range of energies within the gap will exhibit an average value for \( E_a \) determined in this fashion. A larger value of \( E_a \) generally indicates a slower hole release rate and hence a higher likelihood that the detected defect(s) may act as a recombination center(s).

A graph displaying the activation energies and the prefactors \( \nu_0 \) of the defects detected by device type is shown in Figure 4. Four of these \( E_a \) values were deduced from the data shown in Figures 2 and 3, and the others from data on similar cells. The defect response detected in the selenized devices occurred at activation energies ranging from 150 to 250 meV, while the defects detected in the evaporated devices had much smaller activation energies, ranging from 40 to 75 meV. Thus, the defects detected in the evaporated devices have faster carrier release rates and are less likely to be involved in recombination. Moreover, they are more likely to be ionized at room temperature and hence provide additional hole carriers to the device.

The drive-level capacitance profiling (DLCP) technique\(^{16,17} \) was employed to profile the defect density as a function of distance from the materials interface of the CIGS(S) and the adjoining buffer/window layer. DLCP actually determines the depletion region charge density in the vicinity of the location \( x_e \), where this is defined as the location at which \( E_F - E_v = E_e \). Here \( E_F \) is the (quasi) Fermi energy, \( E_v \) the energy of the valence band edge, and \( E_e \) the energy at which the occupation of a gap state can change just rapidly enough to follow the applied alternating bias\(^{16} \) at frequency \( f \):

\[
E_e \equiv k_B T \ln(\nu_0 T^2 / 2\pi f)
\]

which is of the same form as Equation (1) for the activation energy.

**Table II. Semi-quantitative summary of results from AS and DLCP**

<table>
<thead>
<tr>
<th>Device</th>
<th>Estimated free carrier density from AS (cm(^{-3}))</th>
<th>Estimated free carrier density from DLCP (cm(^{-3}))</th>
<th>Estimated trapping state density from AS (cm(^{-3}))</th>
<th>Estimated trapping state density from DLCP (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporated CdS</td>
<td>Low-10(^{15})</td>
<td>Not accessible</td>
<td>Mid-10(^{14})</td>
<td>Not accessible</td>
</tr>
<tr>
<td>Evaporated Cd PE</td>
<td>Low-10(^{15})</td>
<td>Not accessible</td>
<td>Mid-10(^{14})</td>
<td>Not accessible</td>
</tr>
<tr>
<td>Selenized CdS</td>
<td>Mid-10(^{14})</td>
<td>Mid-high-10(^{14})</td>
<td>Mid-10(^{15})</td>
<td>6 \times 10(^{15})</td>
</tr>
<tr>
<td>Selenized Cd PE</td>
<td>Mid-10(^{14})</td>
<td>Mid-high-10(^{14})</td>
<td>Low-10(^{15})</td>
<td>3 \times 10(^{15})</td>
</tr>
</tbody>
</table>

Figure 4. Activation energy and temperature-adjusted thermal emission prefactor of defects from AS studies. The values of \( E_a \) and \( \nu_0 \) are notably larger for the selenized devices (full symbols) than for the evaporated devices (open symbols).
In the special case of one single dominant defect, located at energy $E_e$ from the valence band edge and with trapping density much greater than the free carrier density, $x_e$ is the spatial location at which the defect level crosses the quasi Fermi level. In the DLCP technique, the position of $x_e$ within the sample is varied by adjusting the d.c. bias and the density of carriers responding at the position $x_e$ is determined by analyzing the change in capacitance when the oscillating voltage amplitude is changed. The DLCP signal shows the sum of all states that can respond dynamically to the a.c. perturbation, including both the free carriers and deeper trapping states in the lower-frequency (or higher-temperature) regime. However, at sufficiently low temperatures it is assumed trapping defect states within the bandgap cannot respond, and hence the DLCP response is due solely to the free carrier contribution detected near the edge of the depletion region. Thus, as temperature is decreased, the DLCP density will approach a limiting value that indicates the free carrier density in the $p$-type absorber. At higher temperatures, the trapping defect states also respond. It is assumed that the difference between the maximum and minimum limiting responses at the high and low end of the temperature range of the measurement corresponds to the density of the dominant responding traps $N_t$. The detected states will generally not be interface states. In order for an interface state to contribute to the DLCP response, the defect energy $E_e$ and the quasi Fermi energy at the interface would need to coincide. In the unlikely case an interface state does contribute to DLCP, it would give a distinctive response as the DC bias is varied.\textsuperscript{16}

Typical DLCP data for both types of selenized cell are displayed in Figure 5. Figure 5(a) shows the results from a CdS-buffer cell, and Figure 5(b) from a Cd PE cell. They clearly show the limiting high- and low-temperature responses and can hence be used to estimate the free carrier density $p$ and the density of trapping-state defects $N_t$. The sum of $N_t$ and $p$, labeled $N_{DL_{\text{max}}}$ in Figure 5, is the high-temperature limiting value of the measurement. In Figure 5 the horizontal axis is $\langle x \rangle = eA/C_0$, where $C_0$ is the capacitance value obtained for the lowest amplitude ac voltage limit obtained at a particular nominal d.c. bias.\textsuperscript{16} It is important to note that $\langle x \rangle$ is the average spatial location of the a.c. charge response in the device, and thus it reflects all the responding states—the free carriers at the edge of the depletion region and the response at $x_e$. Consequently, the positions given by $\langle x \rangle$ will typically be intermediate between the defect state(s) responding near $x_e$, and the depletion region edge.

![Figure 5](image-url)  
*Figure 5. Drive-level response of: (a) a selenized CdS device; (b) a selenized Cd PE device. These devices show high- and low-temperature saturation, which allows the trap state density $N_t$ and the free carrier density $p$ to be extracted. The measurement frequency was 11 kHz and the d.c. bias range was 0 to $-1 \text{ V}$.*
The DLCP results for the two selenized devices exhibit a significant difference in defect response as a function of temperature. A measurement frequency of 11 kHz was chosen, because it was high enough to provide good signal-to-noise, and it also allowed us to observe the full defect response above 250 K, but only the carrier response below 160 K. Thus, at this frequency, the convenient 150–300 K temperature range allowed DLCP to span the full range of the possible defect response. From the data plotted in Figure 5, we deduce a free carrier density in the mid-$10^{14}$ cm$^{-3}$ range for both types of selenized devices, a trap density of approximately $6 \times 10^{15}$ cm$^{-3}$ for the selenized CdS device, but a slightly lower trap density (of approximately $3 \times 10^{15}$ cm$^{-3}$) for the selenized Cd PE device. These DLCP trends and values are consistent with the results from AS: the large capacitance step in Figure 3(a), and the somewhat smaller capacitance step in Figure 3(b). The relatively low voltage of the selenized cells is likely the result of the higher defect density and lower carrier density.

The evaporated samples were not conducive to the DLCP analysis shown in Figure 5, because their response showed a steep spatial variation in state density and little variation with temperature. The lack of significant variation of defect response with temperature is consistent with the minimal defect response of AS measurements taken in the same temperature range. Although there was no clear low-temperature limit exhibited by the DLCP data, the lack of temperature variation of the DLCP data, together with the small step in the AS data, indicate that the density of trapping defects affecting these devices is very low. Indeed, the average estimated trap density of these two devices from the AS data was $5 \times 10^{14}$ cm$^{-3}$, nearly an order of magnitude below the selenized devices.

**DISCUSSION**

The results from AS and DLCP measurements described above provide a number of potential reasons for the differences in the performance between the evaporated and selenized devices. First, the significantly lower defect densities in the evaporated devices is likely a primary reason why the evaporated devices have higher $V_{OC}$ values than their selenized counterparts. Indeed, that is consistent with the correlation seen by other groups working on CISS. However, our observations of large defect densities in the selenized CIGSS cells studied are not consistent with reports of significant sulfur passivation of defects in cells made elsewhere.

Secondary ion mass spectrometry (SIMS) measurements of CIGSS devices similar to those used in this study show two specific regions where the sulfur is concentrated, near the very front of the device and near the back of the device (A. Rockett, private communication, 2001). Thus, the lack of observed sulfur passivation in DLCP could be explained if the front region of sulfur concentration occurred closer to the cell interface than $x_e$, the closest distance that DLCP probes. A lower defect density near the interface, however, should affect the raw values of capacitance, and hence show up as a discrepancy between defect densities predicted by AS results and those measured with DLCP. Since the DLCP and AS results for this study are otherwise consistent, we conclude that the sulfur is not a primary factor.

The second significant difference noted between the evaporated and selenized devices is the larger activation energies of the defect response for the latter. In particular the AS results show that holes trapped in the defect band are released at a faster rate for the evaporated compared with selenized absorbers, thus making it less likely that such defects will facilitate recombination. In addition, the shallow activation energies exhibited by the evaporated samples (less than 0.1 eV) suggest that a larger portion of this acceptor band is ionized at room temperature, thus contributing to a higher carrier density in the evaporated devices and an effective trapping state density that is even less than the $3 \times 10^{14}$ cm$^{-3}$ estimated from AS, since those measurements were made at or below 220 K.

**CONCLUSIONS**

This study of the defect properties of CIGS(S) has revealed significant differences in the electronic properties of selenized compared to evaporated absorbers. These differences may help explain corresponding differences in cell performance. Through QE, $J$–$V$ and AS measurements, we have seen that the evaporated-absorber solar
cells produce larger voltages relative to the band gap, have larger fill factors, smaller trapping state densities, lower defect activation energies, and larger hole carrier densities than those fabricated by selenization. Through DLCP, we have confirmed that the trapping state densities of the selenized devices are above $10^{15}$ cm$^{-3}$, similar to results from AR measurements, and significantly larger than for the evaporated cells. The defect differences between the Cds and the partial electrolyte buffers were relatively modest, but those with the Cds buffers were somewhat larger. The quantitative evidence is strongly suggestive that the larger values of Voc in the evaporated-absorber solar cells are a result of not only the larger estimated free carrier density, but also the smaller trapping state densities and the lower defect activation energies.

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