Conduction-Band-Offset Rule Governing J-V Distortion in CdS/CIGS Solar Cells

A. Kanevce, M. Gloeckler, A.O. Pudov, and J.R. Sites
Physics Department, Colorado State University, Fort Collins, CO 80523, USA

ABSTRACT

A type-I ("spike") conduction-band offset (CBO) greater than a few tenths of an eV at the n/p interface of a solar cell can lead to significant distortion of the current-voltage (J-V) curve. Such distortion has been observed in CdS/CIS cells, low-gallium CdS/CIGS cells, and CIGS cells with alternative windows that increase the CBO. The basic feature is reduced current collection in forward bias. The distortion is mitigated by photoconductivity in the CdS or other window layer, and it is therefore more severe if the illumination contains no photons with energies greater than the band gap of the window layer. The device-physics analysis of such distortion is numerical simulation incorporating a three-layer [TCO/CdS/CIGS] approximation for the solar cell. The parameters that influence the barrier height, and hence the distortion, are the magnitude of the CBO, the doping of the p- and n- layers, the defect density of the CdS, and the thicknesses of the CdS and TCO layers. The key value, however, is the energy difference between the quasi-Fermi level for electrons and the conduction band at the CdS/CIS interface. Thermionic emission across the interface will limit the current collection, if the difference exceeds approximately 0.48 eV at 300 K and one-sun illumination. This constraint is consistent with experiment, and strategies to satisfy the 0.48-eV rule when designing solar cells are enumerated.

INTRODUCTION

Thin-film solar cells are promising for energy conversion due to their low cost and good conversion efficiency. Cells with CIGS absorbers have achieved efficiencies of 19.5% [1]. CIGS cells generally use CdS buffer layers, but due to the reduced current collection in the low wavelength region, other alternatives have been proposed. To date, no alternative buffer has achieved efficiency as high as the CdS buffer, but some have come fairly close [2]. To make the search for alternative buffer more successful, it is important to investigate the role of CdS in the cell. One of the features of the CdS/CIS cell can be a deviation from a standard current–voltage curve when the cell is illuminated only with low energy photons. This distortion has been referred to as the “red kink”.

The magnitude of the distortion depends on several parameters, and its dependence on the CdS thickness and on the CdS/CIGS conduction-band offset (CBO) has been investigated experimentally and numerically [3, 4]. The height of the “spike” compared to the conduction band energy in the absorber was proposed as a parameter that determines whether there is a distortion. This work summarizes the dependence of the distortion on additional parameters, provides a physical explanation for the distortion, and introduces a new key parameter that distinguishes well-behaved devices from devices with the J-V distortion.
Figure 1 shows the band diagram of a CIS cell under red-light illumination and zero bias. It shows the conduction-band offset $\Delta E_c$, and the splitting of the Fermi level under illumination into $E_{Fn}$ for electrons and $E_{Fp}$ for holes. The hole current has practically no influence on the distortion, and therefore only the conduction band and quasi-Fermi level for electrons will be analyzed.

**Figure 1.** Band diagram for a CIS device under red-light illumination and zero bias

Assuming thermionic emission across the CdS/CIS interface, the electron current density can be calculated by integrating over the product of carrier density and carrier velocities in the direction of transport $v_x$ [5]. The carrier densities far from the band edge are insignificant and close to $E_c$ the velocities are similar to the thermal velocity, so the integral can be simplified:

$$J_n = q \int_{E_c}^{\infty} v_x dn = qnv_{th},$$  \hspace{1cm} (1)

where $v_{th}$ is the thermal velocity of electrons $\sim 10^7$ cm/s, $q$ is the elementary charge and $n$ is the free carrier density given by:

$$n = N_c \exp[-\frac{E_c - E_{Fn}}{kT}].$$  \hspace{1cm} (2)

$N_c$ is the effective density of states in the conduction band, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. Thus, at a fixed temperature, the maximum electron current through the junction is determined by $n$(CdS) and therefore by the energy difference between the conduction band and quasi-Fermi level for electrons in the CdS close to the interface with CIS. An increase of this energy difference will result in fewer free electrons, and hence in a possible current reduction.

Typical photocurrent densities achieved in the power quadrant for CdS/CIGS cells are $J_L = 32$ mA/cm$^2$. According to equation (1), the minimum carrier density to provide the current flow is $n = 2 \times 10^{10}$ cm$^{-3}$, which corresponds to a 0.48-eV difference between conduction band and quasi-Fermi level. If $E_c - E_{Fn}$ exceeds this value, additional drift fields are required to insure carrier transport across the barrier. This effectively places the main junction under forward bias,
reduces the CIS depletion width and the current collection. For a large barrier, the transport becomes severely limited and collection effectively goes to zero. The 0.48-eV value is calculated for the particular choice of parameters used in the model. Since \( N_c \propto m^*^{3/2} \), a different effective mass choice will alter the 0.48-eV value, but only weakly, since it appears in the logarithmic term. Similarly, the dependence on \( J_L \) is weak. At lower temperatures, the value of \( E_c - E_{F_n} \) needed is smaller, Eq.(2).

**SIMULATIONS**

Numerical simulations were performed with the AMPS-1D software developed at Pennsylvania State University. The three layer model uses a 2.7-μm thick CIS absorber with a band gap of 1.02 eV, a 50-nm thick CdS layer, and a 50-nm thick ZnO layer. Following the suggested baseline [6], the doping densities are \( 2 \times 10^{16} \) cm\(^{-3} \) in the absorber and \( 10^{17} \) cm\(^{-3} \) in CdS. The CdS layer is assumed to be heavily compensated with a defect density of the same order of magnitude as its shallow-dopant density. Several parameters were varied to investigate how they affect the key value \( E_c - E_{F_n} \) and their influence on the observed J-V distortion. The density of acceptor-type defects \( N_{At} \) in CdS was varied between \( 3 \times 10^{16} \) cm\(^{-3} \) (for the well behaved device) and \( 1.5 \times 10^{17} \) cm\(^{-3} \) (for the device with severe distortion). The shallow-dopant density \( N_D \) was varied between \( 4 \times 10^{16} \) cm\(^{-3} \) and \( 1.6 \times 10^{17} \) cm\(^{-3} \). Both of these parameters have a similar effect; the important number is the compensation ratio of ionized dopants \( n \), and midgap acceptor traps \( N_{At} \). The CBO between CIS and CdS is 0.4 eV and assumed to decrease with Ga content. The CBO between CIGS and CdS for the device with 30 % Ga (\( E_g = 1.15 \) eV) is 0.3 eV. The carrier density \( p \) in the absorber was varied between \( 10^{16} \) and \( 3 \times 10^{16} \) cm\(^{-3} \).

**Defect density variation**

The current-voltage curves under red-light illumination for cells with different densities of midgap defects in CdS are shown in figure 2(a). The defect densities are: \( 3 \times 10^{16} \), \( 6 \times 10^{16} \), \( 9 \times 10^{16} \), \( 1.2 \times 10^{17} \) and \( 1.5 \times 10^{17} \) cm\(^{-3} \). In all simulations, the density of ionized donors in the buffer is less than one order of magnitude different than the density of midgap acceptor-type defects. As the defect density increases, the net charge in the depleted buffer becomes less positive, and eventually, for devices that show severe distortion, it becomes negative. The negative charge in CdS creates a barrier for the electrons from the absorber, causing increased recombination in the absorber, which intensifies the magnitude of distortion.

Figure 2(b) shows the difference between the conduction band and quasi-Fermi level for electrons at zero bias and under red-light illumination as a function of position for the lowest defect density (no distortion), medium density (small distortion), and the largest density (severe distortion). It can be seen from figure 2(b), that at zero bias, neither the \( 3 \times 10^{16} \) cm\(^{-3} \) curve nor the \( 9 \times 10^{16} \) cm\(^{-3} \) should be affected, and indeed, close to the spike for both cases, \( E_c - E_{F_n} \) is less than 0.48 eV. The high defect density model predicts significant current restriction even at zero bias, since the \( E_c - E_{F_n} \) value (figure 2[b]) is significantly above the 0.48-eV line. Note that in figure 2 (b) and the others of similar format that follow, \( E_c - E_{F_n} \) always comes close to 0.48-eV at some position even in the non-distorted cases. In these cases, \( E_{F_n} \) will rise sufficiently high to allow 32 mA/cm\(^2\) current, but no higher.
Figure 2. CdS defect density variation. (a) Simulated red light current-voltage curves for defect densities from $3 \times 10^{16}$ cm$^{-3}$ (low) to $1.5 \times 10^{17}$ cm$^{-3}$ (high). (b) Difference between conduction-band energy and quasi-Fermi level for electrons at zero bias and under red light.

CdS thickness

It has been observed experimentally [4], that thicker CdS increases the distortion (figure 3[a]). The midgap defect density of $9 \times 10^{16}$ cm$^{-3}$, which results in a modest kink for the 50 nm thick CdS, was used in the following simulations with varying thickness. The $E_c - E_{Fn}$ difference is shown for +0.3 V and -0.3 V bias. In forward bias (b), the photo-current for all thicknesses is impeded, which corresponds to $E_c - E_{Fn}$ values above 0.48 eV. The effect, however, is small for the thin-CdS sample (solid line). In reverse bias (c), no blocking occurs, and all of the differences are below the 0.48 line, except for the thin spike at the ZnO/CdS interface, which is likely to be eliminated physically by minor inter-diffusion. This example also leads to the conclusion that the current reduction is determined by the $E_c - E_{Fn}$ difference.

Figure 3. CdS thickness variation. (a) Red light J-V curves, Difference between $E_c$ and $E_{Fn}$ for (b) +0.3 V bias and (c) -0.3 V bias
Knowing the mechanism behind the distortion and the parameters influencing it, one can better predict ways to eliminate it. Figure 4 summarizes the combination of defect densities and CdS thicknesses for which a distortion can be expected. An empirical measure of the degree of distortion is the voltage difference at 1/2 J_{sc} between a well behaved device and one with distortion. Devices where this difference is lower than 0.05 V are considered well behaved, if the difference is between 0.05 and 0.45 V the distortion is “modest”, and devices that have a difference higher than 0.45 V are called “severe” distortion devices. A typical CIS cell falls in the “modest” distortion region. It can be seen that the distortion can be eliminated by thinning the CdS layer, or by decreasing the defect density in CdS. In practice, the distortion is generally eliminated in a third way, by the photoconductivity induced by the blue photons that increases electron density and hence narrows the E_c - E_{Fn} difference in the CdS layer.

![Figure 4](image)

**Figure 4.** Dependence of the distortion on the CdS thickness as well as on the N_{At} (midgap acceptor-type defect density in CdS).

**CBO variation**

Theoretical predictions show that replacing In with Ga increases the band gap mostly through the conduction band \[9\], and, hence, the CBO decreases as the band gap increases. The distortion is strongly dependant on the conduction-band offset. Two examples are taken to illustrate the dependence of the distortion on the Ga content. Figure 5 shows E_c – E_{Fn} in the CdS at the CdS/CIGS interface for CIS model with a band gap of 1.02 eV (CBO ≈ 0.4 eV), and a CIGS model, with 30% Ga and a band gap of 1.15 eV (CBO ≈ 0.3 eV). For the well-behaved device, the difference between the conduction band and quasi-Fermi level decreases with the applied bias. For devices that show distortion, this difference starts to increase exactly at the voltage bias where the onset of current impedance appears. As expected, the distortion is much more severe for higher CBO (no Ga).

Other parameters investigated show weak or no influence on the distortion. For example, an increased absorber carrier density shows slightly stronger distortion, although the influence was much weaker than for CdS parameters. This is because increased CIGS doping shifts more band-bending toward the CdS and therefore a larger E_c – E_{Fn} at the CdS/CIGS interface is expected. The TCO thickness had practically no influence on the distortion. Both of these observations are in good agreement with 0.48-eV rule.
Figure 5. $E_c - E_{Fn}$ for (a) CIS cell and (b) CIGS cell with 30 % Ga

CONCLUSIONS

The key parameter behind J-V distortions in CdS/CIGS cells, $E_c – E_{Fn}$ at the interface, has been identified and quantified. With minor numerical changes it should be applicable to other heterojunction systems. Reducing the problem to this key parameter allows discussion independent of material properties. It might allow quantification of interface properties once applied to specific devices. Although a specific set of parameters was used in this work, the general strategy should equally apply for other configurations.

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