Current Transients in CdS/CdTe Solar Cells

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ABSTRACT

Current transient responses to voltage and illumination steps are investigated to elucidate the mechanisms involved in carrier transport in CdS/CdTe cells. For most cells, the response to a dark, forward-bias step after a long dark soak at zero bias is a current growth curve. For one such cell, the magnitude of the transient is ≈ 22% of the starting value with half of the growth occurring within ≈ 10 sec, the other half requiring 1000's of seconds. The effect is completely reversible and a mirror-image decay curve at zero bias after dark bias-on equilibration can be measured. Similarly, a complex of growth and decay curves are observed on application of illumination steps with constant bias. Similar transients have been observed by McMahon [1] and del Cueto et al. [2]. This paper is a survey of these effects in cells from 3 different fabricators.

These transients, with varying magnitudes and directions, were seen in all the cells studied. In general, the better the cell, the smaller the magnitudes of the transients. They range from changes by factors of 10 for pathological cells to subtle fast transients (1-2%) in excellent cells.

Beside the important implications these transients have for accurate measurements of cell efficiency and stability, they provide clues about the carrier transport mechanisms. One of the mechanisms proposed involves the occupation of deep donor traps with small hole cross sections, changing their recombination kinetics. The second hypothesis involves the modulation of the junction barrier profile by changing the charge on deep acceptors and donors by carrier trapping, leading to a change in the effective junction barrier height. A third involves defect mutation such as that of [Cu] donors into [VCd-Cu] acceptor complexes, depending on the position of the quasi-Fermi levels.

INTRODUCTION

Although measurement of transients is straight-forward, attributing them to a mechanism and location in the cell is not. Many time constants apply to an electrical or light step response:

<table>
<thead>
<tr>
<th>MECHANISM</th>
<th>TIME CONSTANT (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier thermalization within bands</td>
<td>10¹</td>
</tr>
<tr>
<td>Recombination lifetime</td>
<td>10⁻⁴ to 10¹</td>
</tr>
<tr>
<td>RC time constant for 1 cm² cell &amp; 100 Ω</td>
<td>10² to 10⁴</td>
</tr>
<tr>
<td>C-V response for shallow states ≈ 1 MHz</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>C-V response for deeper states ≈ 100 Hz to 30 kHz</td>
<td>3 x 10⁻⁵ to 10⁻²</td>
</tr>
<tr>
<td>Trapping and detrapping times</td>
<td>10⁻⁶ to 10⁻⁴</td>
</tr>
</tbody>
</table>

When bias (or light) is suddenly applied to a device, the initial dark current (or light-generated current, J_L) change will occur in times on the order of the recombination lifetime or the RC time constant. Then the occupancies of the conduction and valence bands and the gap states readjust themselves by mechanisms like carrier trapping and defect state mutation toward some steady state. The readjustment can cause changes in the cell current by changing the band profile and/or the recombination losses. This survey is focused on currents in the trapping time region.

EXPERIMENTAL DETAILS

Dark current growth transients were measured by sudden application of a forward-bias step (e.g., 0.65 V), after a dark, zero-bias equilibration period of 0.5 to 10 hours at RT called here the "dark soaked" or "DS" state. In most cases continued application of forward bias increases the current asymptotically toward a "forward-bias-soaked" or "FBS" state. The effect is completely reversible, with a decay to the DS state. The current/time data were taken using an HP 7090A A/D buffer input recorder with a 30 k/sec sampling rate (rise times < 0.01 sec could be measured.
reliably). J-V data was recorded point by point, holding the bias constant with dwell times of 3 to 10 sec at each bias, using a red (630 nm) LED with an output equivalent to ≈ 1 sun for light data. Red (630 nm) and blue (470 nm) LEDs were used for light transient measurements, usually with an equivalent photon current density \( J_{ph} \) of ≈ 1.4 mA/cm\(^2\). The major part of the blue was absorbed by the CdS, with low quantum efficiency \( QE \), so that \( J_{sc} \approx 0.3 \) mA/cm\(^2\). All of the red was absorbed only by the CdTe close to the junction, so its \( QE \) was larger, \( J_{sc} \approx 1.2 \) mA/cm\(^2\).

**DISCUSSION**

**J-V Characteristics – CSU Cells**

The J-V characteristics of the cells varied a great deal between fabricators and treatments. However, the CSU (Sampath) unstressed and stressed cells were very much the same. Both CSU cells showed a gradual irreversible increase in the lower portion of the log J-V curves Fig. 1a, which didn’t affect their \( ff \) or \( Voc \). Both these cells were exceptional in that there was almost no cross-over. These data (Fig. 1b) suggest that the forward-bias transport is not altered appreciably by illumination; the light curve appears to be simply a dark curve displaced downward by the bias dependent light-generated current density \( J_L(V) \) (which might be called quasi-superposition).

![Figure 1. CSU stressed cell: a) evolution of log J-V over time  b) linear J-V showing \( J_L(V) \).](image_url)

**J-V Characteristics – IEC Cells**

One of the IEC cells had Cr contacts without Cu and the other had Cu-Cr contacts and showed very different behavior (Fig. 2 a and b). The extreme roll-over for the no-Cu cell suggests a high back contact barrier height (\( \Phi_{bc} \)) and low effective acceptor density (\( N_a - N_d \)) where \( N_a \) and \( N_d \) are the shallow acceptor and donor densities.

**J-V Characteristics – NREL Cells**

The NREL cells were processed with less-than-, equal-to-, and more-than-optimum Cu, but otherwise identically. The \( Cu < opt \) cell suffered from poor collection and \( \approx -2 \) V reverse bias was required to pull out the appropriate \( J_L \) (Fig. 3 a and b). This suggests that \( (N_a - N_d) < 0 \), or at least the front portion of the CdTe layer, and that the front portion of the bands in the CdTe layer are bent concave upward. The \( Cu>opt \) cell had the kind of +, –, + curvature seen in the AMPS [3] modeling of an n-CdS/i-CdTe/p-CdTe/i-CdTe junction with a large \( \Phi_{bc} \).

**Dark Forward Bias Transients**

For most of the cells, the transient current response \( (\Delta J(V_f)) \), following a constant dark, forward-bias step \( (\Delta V_f) \) and after a long dark soak at zero bias (DS), is a growth curve. The initial, instantaneous step as the bias is turned on \( (<0.01 \) sec) is not included in \( \Delta J(V_f) \). For example (Fig. 4a), the magnitude of the transient is \( \approx +22\% \) of the starting value. The effect is completely reversible and a mirror-image decay curve at zero bias after dark bias-on equilibration can be measured using short \( (0.2 \) sec) pulses of \( V_f \) as a probe.
Figure 2. IEC cells with a Cr contact and a Cu + Cr contact: a) log J-V, b) linear J-V.

Figure 3. NREL cells 669B-4, 664B-3, and 665B-4

All of the cells have similar transients, but with different magnitudes and directions of growth or decay. A summary is given in Table 1. The ratio of ΔJ(Vf) to the initial J appears to reach a maximum at Vf = 0.6 to 0.7 V. For all the cells, the decay/growth data could be reasonably fit by (a) a sum of exponential growths with time constants ranging from 0.1 to > 400 sec, (b) a stretched exponential, suggesting a distribution of trapping energies, or (c) log(t) for growth and log(1/t) for decay (for most of the central time span).

Similar growth and decay curves are observed with weak illumination before or during the ΔVf step. In one case, the NREL Cu<opt. cell, red light reversed the decay to a growth. At V = 0 all the cells on application of red and/or blue illumination pulses, produce flat bottomed square pulses with no discernable decay or growth of Jsc, i.e., ΔJ(Vf) = 0 (except Cu < opt, which had a slight decay with red light).

Light Forward Bias Transients

For the CSU unstressed cell all the rise and fall times were shorter than 0.01 sec except for red plus blue illumination (Fig. 4b) at Vf. The first part of the growth curve is exponential, with a time constant of about 0.14 sec, much faster than the dark ΔJ(Vf) transients above. For the CSU stressed cell, all the light pulse transients rise times were < 0.01 sec and ΔJ(Vf) = 0.

For the IEC cell with the Cr-only contact, at Vf = 0.7 V there was a rich assortment of pulse transients (Fig. 5a). Note that the current is reduced with light on, in contrast with the NREL cells.
Table 1. Properties of various cells

<table>
<thead>
<tr>
<th>CELL</th>
<th>CONDITION</th>
<th>DARK $\Delta J(V_f)$</th>
<th>LIGHT $\Delta J(V_f)$</th>
<th>RED $\Delta J(V_f)$</th>
<th>BLUE $\Delta J(V_f)$</th>
<th>COMMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSU 15244-1</td>
<td>unstressed</td>
<td>+ 22% R</td>
<td>+ 20- 30% R</td>
<td>flat reduction by $J_1(V)$, no transient</td>
<td>reduction by $J_1(V)$, $\Delta J(V_f) = 0$</td>
<td>Blue or red had no effect on $\Delta J(V_f)$</td>
</tr>
<tr>
<td>CSU 15244-9</td>
<td>stressed</td>
<td>+ 50% R</td>
<td>+ 50% R</td>
<td>flat reduction by $J_1(V)$, no transient</td>
<td>reduction by $J_1(V)$, $\Delta J(V_f) = 0$</td>
<td>Blue or red had no effect on $\Delta J(V_f)$</td>
</tr>
<tr>
<td>IEC VT128-4</td>
<td>Cr only</td>
<td>- 50% R</td>
<td>- 10% R</td>
<td>flat reduction by $J_1(V)$, no transient</td>
<td>$\Delta J(V_f) = 0$</td>
<td>Blue light increased dark $\Delta J(V_f)$ to 20%NR</td>
</tr>
<tr>
<td>IEC VT128-3</td>
<td>Cr + Cu</td>
<td>+5% R</td>
<td>+ 25% red R</td>
<td>flat reduction by $J_1(V)$, no transient</td>
<td>$\Delta J(V_f) = 0$</td>
<td>Blue light increased dark $\Delta J(V_f)$ to 20%NR</td>
</tr>
<tr>
<td>NREL 699B-4</td>
<td>Cu &lt; optimum</td>
<td>- 25% R</td>
<td>+ 25% w. red R</td>
<td>13 x growth &amp; ramp up R</td>
<td>10x growth &amp; slow ramp up R</td>
<td>Red light reversed dark $\Delta J(V_f)$ to + 25% R</td>
</tr>
<tr>
<td>NREL 694B-4</td>
<td>Cu = optimum</td>
<td>+ 6% R</td>
<td>+6% w. blue R</td>
<td>flat reduction by $J_1(V)$, no transient</td>
<td>reduction by $J_1(V)$, $\Delta J(V_f) = 0$</td>
<td>Blue light increased dark $\Delta J(V_f)$ to 6% R</td>
</tr>
<tr>
<td>NREL 695B-3</td>
<td>Cu &gt; optimum</td>
<td>± 6% R</td>
<td>± 2200% w. blue R</td>
<td>22 x growth &amp; complex waveform Fig. 6a R</td>
<td>400 x growth &amp; complex waveform not shown R</td>
<td>$\Delta J(V_f)$ + for $V_f &lt; 0.65$, - for $V_f &gt; 0.65$. Huge photosensitivity</td>
</tr>
</tbody>
</table>

$\Delta J(V_f) = 100 \times (J_{max} - J_{min})/J_{start}$, where $J_{start} = J_{min}$ for growth and $J_{start} = J_{max}$ for decay. Positive is growth when bias is turned on, negative is decay. R = reversible, NR = not reversible

Figure 4. (a) $\Delta J(V_f)$ decay and recovery data for unstressed CSU cell (#15244-1). The stressed cell data are quite similar. Both curves calculated using the same stretched exponential parameters: time constant = 15 sec and stretch parameter = 0.35. (b) Transient for same cell.

below. When blue or red illumination is turned off, the dark current is increased temporarily, but decays rather quickly to a steady dark value. This decay is much faster and closer to exponential than the dark $\Delta J(V_f)$ discussed above. They are superimposed on the slower dark $\Delta J(V_f)$ decay which resumes from where it left off before the light pulses. They appear to be separate processes.

Infrared Quenching

The literature indicates that photoconductivity in the CdS layer, known to have high concentrations of Cu, influences the carrier transport. One of the common signatures of CdS:Cu photo-conductors is infrared quenching in two principal bands: 720 - 1000 nm and 1300 - 1660 nm. Exposure to $\leq 510$ nm light enhances the photoconductivity of previously quenched samples. The cells were exposed to combinations of red, blue, and ir (940 nm at $\approx 4$ mW/cm$^2$) sources and $\Delta J(V_f)$ was measured at $V = 0$ and $V$ near $V_{oc}$. No indication of quenching by the ir was observed for any of the cells, except for NREL Cu < opt. which showed a +10 µA increase in current at $V_f = 0.6$ V, rather than its normal $I_{sc} = -3$ µA.
Figure 5. (a) IEC Cr only cell, response to red + blue. (b) NREL Cu < opt. cell. V.

Figure 6. NREL Cu > opt. blue incident power in µW/cm²: a) transients, b) log J-V data

The currents for a number of cells showed apparent enhancement by blue light, however.

DISCUSSION

Since all the transients occur at currents in the linear region of the log J-V curves (except for the NREL Cu < opt.), well below the part influenced by "series resistance" effects, the transients appear to be properties of the main junction. This view is supported by the “dark” log J-V data for the NREL Cu > opt. cell, Fig. 6b, taken with very weak bias light.

It appears that the application of bias in the dark moves the quasi-Fermi levels (E_{fn}, E_{fp}) through a density of trapping states in the CdTe, and, for the growth transient, holes are trapped at deep acceptors, making the material more n-type and moving the bands down. This decreases the barrier for the forward-bias electron current and increases J. Since the movement of the E_{fp} with respect to the trap levels is largest near the CdS/CdTe interface, especially for larger (N_d – N_a), it seems more likely that the relevant hole traps would be there and that the growth would be larger for smaller (N_d – N_a). Electron traps would be relevant for the decay situation.

In Fig. 5a, it is clear that the dark current is increased above its dark equilibrium value by the prior illumination pulses. It then decays to its dark quasi-equilibrium value when the light is turned off, over a period of 5 to 10 sec. The currents are small enough so that cell heating is not an issue. AMPS [3] modeling shows that the principal difference between blue and red illumination is that the hole density in the CdS and at the CdS/CdTe interface increases by many orders of magnitude with blue light; the carrier densities elsewhere are virtually unchanged. A possible explanation is that the conduction band (CB) in the CdS and/or at the CdS/CdTe interface is moved up and down by carrier trapping there, changing the junction transport.

The NREL Cu = opt. cell responded to light with flat bottomed pulses, with J simply being reduced by J_l(V).

However, the NREL Cu < opt reacted to red (0.1 mA photon current) at V = 0.6 V, by the
current increasing by factor of 13 immediately and then continuing to ramp up as log(t) (Fig. 5b). For blue (also 0.1 mA), the initial increase was ≈ 7 x and the ramp was slowly up. In a similar vein, the slopes of the only the blue and blue + red pulses for the IEC Cr-only cell in Fig. 5a are always positive while the only-red-on are negative. Blue pulse response for NREL Cu>opt. Fig. 6a shows a large photoconductivity gain with very weak blue light. The effect of blue bias light on the “dark” log J-V curves (Fig. 6b) again suggests that these are main junction effects.

This points to a photo-gating effect and suggests that the blue light generates a high density of both electrons and holes in the CdS, and when the holes are trapped, the CdS becomes more n-type. Its electric field is reduced and so is the QE. The portion of JL photo-generated in the CdS is reduced, so the total current goes up. In addition, the interface recombination loss of photo-generated carriers is increased, also causing the net current to go up. A similar mechanism is found for the “red kink” effect in CIGS cells by Pudov et al. [4].

The red light generates carriers only in the CdTe, and because the CdS VB is a large barrier to holes, mainly electrons are injected into the CdS, emptying the hole traps and making the CdS less n-type. Its electric field is increased and the loss of carriers to interface recombination is reduced, so the total current goes up.

CONCLUSIONS
All the cells showed dark forward bias transients, but their magnitude and direction depends on cell preparation. In every case, the transients are reversible and the transient and its recovery can be fit approximately by log(t) for growth and log(1/t) for decay. Bias and light induced transients are small for cells which are well behaved, without roll-over and cross-over.

Cells with pronounced roll-over and cross-over show larger transients. Because (a) in most cases the entire log J-V curve is affected, and (b) Vf was chosen in the linear portion of the log J-V curve, the data indicates that the transients are a property of the main junction rather than “series resistance” effects.

The roll-over and cross-over cells also show large, short term (seconds) transients in response to blue (470 nm) and red (630 nm) light pulses, which appear to result from trapping in the bulk of the CdTe (630 nm) or in the CdS layer or theCdS/CdTe interface (470 nm).

None of cells show the infrared quenching typical of CdS:Cu photoconductors. However, the roll-over and cross-over cells do show enhancement of forward bias current under blue light, which is also typical of CdS:Cu.

Mechanisms involving trapping of electrons and/or holes in the bulk of the CdTe, the CdS/CdTe interface, and/or the CdS layer have been postulated. The forward-bias transients are a general feature of all of the cells. The mechanisms, in particular the location and type of trapping, are more specific to each of the cells. More specific research is needed to identify and characterize the mechanisms involved.

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REFERENCES
3. AMPS-1D, written by S. Fonash, Pennsylvania State Univ., supported by EPRI.