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THE USE OF 2ND AND 3RD LEVEL CORRELATION ANALYSIS FOR STUDYING DEGRADATION IN POLYCRYSTALLINE THIN-FILM SOLAR CELLS

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ABSTRACT

The correlation of stress-induced changes in the performance of laboratory-made CdTe solar cells with various 2nd and 3rd level metrics is discussed. The overall behavior of aggregated data showing how cell efficiency changes as a function of open-circuit voltage (Voc), short-circuit current density (Jsc), and fill factor (FF) is explained using a two-diode, PSpice model in which degradation is simulated by systematically changing model parameters. FF shows the highest correlation with performance during stress, and is subsequently shown to be most affected by shunt resistance, recombination and in some cases voltage-dependent collection. Large decreases in Jsc as well as increasing rates of Voc degradation are related to voltage-dependent collection effects and catastrophic shunting respectively. Large decreases in Voc in the absence of catastrophic shunting are attributed to increased recombination. The relevance of capacitance-derived data correlated with both Voc and FF is discussed.

INTRODUCTION

Polycrystalline CdS/CdTe thin-film solar cells have demonstrated small-area, laboratory efficiencies of 16.5% [1]. The highest published efficiency for CdTe modules is 11.1% [2]. In addition to considerable research addressing addressing efficiency, recent work has focused on understanding the durability of these thin-film semiconductor devices. The effects of back contact and processes on cell durability have been discussed for example in [3-5]. More recently, the detrimental effects of localized shunts [6], the general effects of film micro-nonuniformities [7], and the effect of cell-fabrication processing through formal design-of-experiments methodologies [8] have been reported.

The basic structure of a thin-film CdS/CdTe solar cell is that of a glass superstrate design in which light passes through a conducting/insulating (buffer) oxide film layer stack deposited on glass. Tin oxide (SnO₂) is the most common transparent conducting oxide (TCO), though there is considerable interest in the stannate compounds (Cd₂SnO₄ and SnZnOₓ) for their superior optical properties [1].

Once transmitted through the glass/TCO/buffer superstrate, light is absorbed in the n-CdS/p-CdTe heterojunction structure, which provides the field necessary for charge separation. A back contact structure completes the cell. A schematic of this basic design is shown in Fig. 1.

Figure 1 Basic CdS/CdTe solar cell design.

To ascertain durability, cells were fabricated and then exposed to 1-sun illumination under open-circuit, Voc, bias and acceleration temperatures of 60 – 120 ºC for times exceeding 1000 hours [9]. Two dominant degradation mechanisms were identified in the temperature range studied. As shown in Fig. 2(a), from 60-80 ºC, an activation energy of 2.94 eV was measured and was attributed to S-outdiffusion from the CdS layer into the CdTe based on a reported value of 2.8 eV for bulk diffusion of S in CdTe [10]. This assertion was also supported by the observation of Kirkendall voids in the CdS layer. In the temperature range 100-120 ºC, an activation energy of 0.63 eV was determined, in good agreement with the reported value of 0.67 eV for Cu diffusion in CdTe [11].

Figure 2 Degradation activation energies (a) and how the linear correlation (R²) of Δη% changes with Voc, Jsc, and FF as a function of stress temperature (b).
Since cell efficiency, η%, is determined by the equation:

\[ \eta\% = \frac{V_{oc} \times J_{sc} \times FF}{\Phi_{inc}} \]

(where Φ_{inc}, the incident power density, is typically normalized to a solar value of 100 mW/cm²), a comparison of the linear correlation coefficients of ∆η% versus changes in V_{oc}, short-circuit current density, J_{sc}, and fill factor, FF, during stress testing as a function of stress temperature was performed. This analysis is shown in Fig. 2(b). The moderate correlation of η% with J_{sc} seen at lower stress temperatures is due to reduced optical attenuation associated with S-outdiffusion from the CdS. The most important variable affecting η% at all temperatures, approaching an ideal value at 120 ºC, was FF.

Similar trends are observed when looking at aggregate cell stress data. Figure 3 is a plot of the percent change in efficiency (del Eff) vs. changes in V_{oc}, J_{sc}, and FF (del V_{oc}, del J_{sc}, and del FF, respectively) obtained in a set of 2052 measurements performed on CdTe devices stress tested at NREL with no regard to subtle changes in processing or stress conditions.

The strong correlation of decreasing η% with both V_{oc} and FF is obvious, as is the general lack of correlation with J_{sc}. These figures also show possible annealing effects resulting in improved performance through increasing FF as well as the general observation that J_{sc} often increases during stress testing.

In this paper, through a combination of modelling and the examination of past data, we hope to provide a better understanding of why these correlations are observed between performance and changes in V_{oc}, J_{sc}, and FF.

**J-V Curve Modeling**

PSpice modeling provides an easy method by which to understand basic solar cell behavior. In Fig. 4, a parallel combination of forward-biased diodes is used to independently simulate recombination currents in the quasi neutral (J_{QNR}) and space charge (J_{SCR}). The back contact behavior is represented by the parallel combination of a reverse-biased diode (J_{b}) and shunt conductance (1/R_{sh}) that was previously used to model performance characteristics observed in the first quadrant [12]. The theoretical basis for the two-diode model as a general expression for the current produced in a solar cell can be found in Ref. [13].

\[ J = J_{SCR} + J_{QNR} + \left( \frac{V - JR_s}{R_sh} \right) - J_{ph} \]  

(2)

where J_{SCR}, J_{QNR}, and J_{ph} are the recombination currents and photo generated current respectively, while R_{s} and R_{sh} represent series and parallel (shunt) resistance losses. J_{SCR} and J_{QNR} are further represented by the following:

\[ J_{QNR} = J_{01} e^{(V - JR_s)/kT} - 1 \]  

(3)

\[ J_{SCR} = J_{02} e^{(V - JR_s)/2kT} - 1 \]  

(4)

where J_{01} and J_{02} are further dependent upon minority carrier transport properties.
In the fourth quadrant, maximum power output is achieved by maximizing the term, $J_{ph}$, and minimizing the first three terms in (2), often referred to collectively as the “forward” current. Each of the forward current terms contributes to decreased cell performance. It should be noted that the recombination currents, $J_{QNR}$, and $J_{SCR}$ are themselves dependent on resistive effects as shown in (3) and (4).

Using the J-V curve measured for a 14.4% cell fabricated at NREL, the percent that each parameter contributes to the forward current (and thus loss) in the power quadrant was determined and is shown in Fig. 5. This calculation used a fit-determined value of 3 Ω·cm$^2$ for $R_s$ which is a reasonable upper value observed during stress testing of these cells [9].

Figure 5 Forward current contributions to loss.

As seen in this figure, recombination occurs mostly in the space charge near $V_{oc}$ where recombination in the quasi neutral region, i.e., between the depletion width and back contact, begins to dominate. Note that resistive contributions for both effectively go to zero at $V_{oc}$ where $J = 0$ in equations (3) and (4). The voltage, $V$, at which $J_{QNR}$ exceeds $J_{SCR}$, is given by the relation:

$$V = \frac{2kT}{q} \ln\left(\frac{J_{02}}{J_{01}}\right)$$

(5)

In high efficiency cells (smaller $J_{02}$) with higher $V_{oc}$ values, the $J_{01}$ term has a strong effect on $V_{oc}$. It is primarily for this reason that a two-diode model is preferred over one-diode models in which an “average diode factor (typically between 1 and 2) is usually determined. In general, if $V_{oc}$ is less than 800 mV, the importance of $J_{01}$ is reduced.

RESULTS AND DISCUSSION

Cell degradation during stress can be modeled by changing the discrete elements of Fig. 4. Increased recombination ($J_{01}$, $J_{02}$), resistive losses (increasing $R_s$, decreasing $R_{sh}$), and degraded backcontacts (decreasing $J_b$ due to an increase in $E_b$, increased $R_b$) all cause performance to decrease. These effects on both the J-V characteristics of cells, and performance correlations similar to those shown in Fig. 3 were determined using PSpice as a modeling tool. For the sake of brevity, only important results explaining the behavior shown in Fig. 3 will be presented. An initial “baseline” cell with $J_{01}=3\times10^{-15}$ A/cm$^2$, $J_{02}=1\times10^{-09}$ A/cm$^2$, $R_{sh} = 200$ KΩ·cm$^2$, and $R_s = 3$ Ω·cm$^2$ was used as the point from which degradation in $V_{oc}$, $J_{sc}$, FF, and η% were determined.

Back contact degradation

A commonly observed degradation characteristic of CdTe solar cells is the formation of “roll-over” in the 1st quadrant. As mentioned previously, this effect can be modeled through introducing a contact diode leakage current, $J_b$ which is inversely related to the back contact barrier height $E_b$ [12]. Graphically, $J_b$ can be estimated as the current at which the J-V curve “rolls over” in the 1st quadrant. For our simulations, a “baseline” value of $E_b = 0.56$ eV (which equates to $J_b\approx10$ mA/cm$^2$) and a value of $R_b = 0$. When $R_b=0$, the barrier is effectively absent in the 1st quadrant however it’s appearance with degradation (as well as with low-temperature J-V measurements) confirms it’s presence. Simulations were performed with $E_b$ increasing to 0.68 eV ($J_b\approx0.1$ mA/cm$^2$) and $R_b$ increasing as high as 100 Ω·cm$^2$.

The correlation of del Eff vs. del $V_{oc}$, del $J_{sc}$, and del FF assuming a nominal setting of $R_b$ equal to 5 Ω·cm$^2$ is shown in Figure 6.

Figure 6 Efficiency change with contact barrier increase.

Figure 6 (and subsequent figures) has been scaled to allow comparison with Fig. 3. As seen in Fig. 6, a change in the back contact diode behavior only affects efficiency through FF. As the contact degrades, it affects neither $V_{oc}$ nor $J_{sc}$. The increase in $E_b$ shown in Fig. 5 is a worse-
case estimate as 1\textsuperscript{st} quadrant behavior typically does not show such roll-over. The decrease in $\eta%$ shown in Fig. 6 is thus not large enough to explain the $\eta%$ vs. FF behavior shown in Fig. 3(c).

**Resistive effects ($R_{sh}$, $R_s$)**

Decreasing shunt resistance, $R_{sh}$, is a strong root cause for the behavior shown in Fig. 3(c). $R_{sh}$ begins to affect FF as it approaches ~ 1000 $\Omega \text{cm}^2$, and $V_{oc}$ and $J_{sc}$ at a level closer to 100 $\Omega \text{cm}^2$. The correlation of del Eff vs. del $V_{oc}$, del $J_{sc}$, and del FF as $R_{sh}$ decreases is shown in Figure 7.

![Figure 7 Efficiency change with decreasing $R_{sh}$.

Values of $R_{sh}$ as low as 50-100 $\Omega \text{cm}^2$ can be observed during cell stress testing and can account for the large performance drops observed in Fig. 3. In cases of extreme shunting, $J_{sc}$ can degrade by as much as 10%. The sharp increase in $V_{oc}$ degradation occurring in extreme shunting (what might be referred to as catastrophic degradation) is also reflected in Fig. 3(a) where the rate of $V_{oc}$ drop begins to increase greatly at a decreased performance level of ~40%.

A similar plot of the effect of series resistance, $R_s$, is shown in Fig. 8.

![Figure 8 Efficiency change with increasing $R_s$.

Similar to $R_{sh}$, $R_s$ can have a strong effect on FF, but differs in that it has no effect on $V_{oc}$, and only a very slight impact on $J_{sc}$ at very high degradation levels. In practice, $R_s$ is not observed to increase much from baseline levels and thus $R_{sh}$ is believed to be more important in determining FF during stress testing.

**Recombination**

The effect of back contact and resistive degradation shown in Figs. 6, 7, and 8 do not adequately explain features observed in Fig. 3(a) and 3(b). Of these, only very large catastrophic decreases in $R_{sh}$ (Fig. 7) can explain some of the large changes in $V_{oc}$ and $J_{sc}$ shown in Fig. 3. However, such changes are frequently observed in cells that do not exhibit "catastrophic" shunting.

Increased recombination was modeled by systematically increasing $J_0$ from its baseline value of $1e^{-09}$ to $1e^{-06}$ $A/cm^2$. The corresponding correlation plot is shown in Fig. 9.

![Figure 9 Efficiency change with increasing $J_0$.

An order magnitude increase in recombination current can account for most of the observed decrease in $V_{oc}$ shown in Fig. 3(a) as well as a portion of the decrease in FF seen in Fig. 3(c). The fact that $V_{oc}$ degrades during stress testing cells is a clear indicator of the importance in mitigating recombination in order to achieve stable cells.

As mentioned previously, significant decreases in $J_{sc}$ have been observed where catastrophic shunting is not observed. Yet, the modeling performed with PSpice cannot explain this. The reason for this is due to the inability of PSpice to model a well-known effect in polycrystalline thin film cells known as voltage-dependent collection [14].

In PSpice simulations, this additional loss mechanism can be captured by properly adjusting the resistive model parameters. At $V=0$, the slope of the J-V curve can be used to accurately determine $R_{sh}$. The 1\textsuperscript{st} quadrant behavior can then be used to adjust $R_s$ in the absence of roll-over. If the latter is present, $R_s$ can still be determined by fitting the curve between the maximum power point, $P_{max}$ and $V_{dc}$. In doing so, voltage-dependent collection is
revealed as the difference between the model fit, and the actual J-V curve. Figure 8 is an example of this procedure applied to a cell where after 722 h of stress, η% had decreased 33% with a corresponding decrease in J_sc of 4.8%. In this example, neither R_sh (fixed by dV/dJ at V=0, or R_s (fixed by dV/dJ in the 1st quadrant) could adequately model the drop in J_sc. A comparison between the best model fit and the actual J-V curve is shown in Fig. 10.

Figure 10 Voltage-dependent collection

The difference observed between the model-determined fit and the actual J-V curve after 722 h of stress (T = 125 °C, Voc bias, 1-sun illumination) is believed to reveal an additional voltage-dependent loss mechanism (not present at t=0) beyond recombination as represented by equations (3) and (4). No iteration of the discrete element parameters of the model shown in Fig. 4 can replicate the actual J-V curve. For the cell shown in Fig. 10, the additional voltage-dependent degradation introduced into the cell by stress testing corresponds to approximately a 0.96% and 3.78% increase in Jsc and FF loss, respectively.

3rd-Level Metric Correlations

The previous approach to understanding degradation requires little more than measuring and modeling details associated with J-V curves. In some measure, the incorporation of recombination terms provides a slight foray into more complex, higher-order parameters often extracted by sophisticated metrology tools and techniques. Unfortunately, the latter tools are often expensive and not readily available to those requiring many measurements in order to reach statistically viable conclusions. The techniques themselves often suffer from being too time-consuming or are entirely destructive or requiring ambient conditions that might introduce degradation not characteristic of field degradation in the cell. In order to increase our ability to probe for changes occurring in cells and modules during stress testing, we have recently developed and reported on the use of bi-directional voltage scans during capacitance measurements to both understand degradation [15] as well as to study and improve upon module stabilization procedures [16].

In Ref. [15], the relative durability of CdS/CdTe cells grown on either a bi-layer SnO₂ or cadmium/zinc stannate (CTO/ZTO) superstrate was evaluated. Cells grown on the latter typically exhibit greater Voc and FF degradation than cells grown on the more common SnO₂-coated substrate. Using the two-direction, voltage scan method, capacitance-voltage (C-V) hysteresis in cells was determined as a function of stress time. Hysteresis is arbitrarily defined as the difference in Wd at V = 0 between reverse and forward direction scans, i.e., Wd,rev − Wd,fwd . Fig. 11 summarizes the variation of hysteresis with stress time as well as the correlation of both Voc and FF with hysteresis determined in this study.

Figure 11 Variation of C-V hysteresis with stress time (a) for cells based on TCO-type and subsequent correlations of (b) Voc and (c) FF with hysteresis. The increased hysteresis shown in Fig. 11(a) was paralleled by a decrease in performance during stress. The correlation of hysteresis with both Voc and FF (shown in Fig. 8(b) and 8(c), respectively) is also apparent. The correlation coefficient, R², of Voc with hysteresis for
CTO/ZTO cells #1 and #2, and SnO₂ cells #1 and #2, were 0.98, 0.46, 0.75, and 0.82, respectively. The same values for FF were 0.99, 0.58, 0.63, and 0.87, respectively. Similar analysis performed without considering hysteresis, i.e., based on either \( W_{d,fwd} \) or \( W_{d,rev} \) separately were not nearly as high and tended to show non-monotonic behavior.

As discussed in Ref. [16], finished thin-film modules (including those based on Cu(In,Ga)Se₂) exhibit various degrees of hysteresis. The trends shown in Fig. 11 are in some cases replicated by the observations made on modules undergoing various tests to determine procedures to achieve stabilization prior to benchmarking performance. Figure 12 shows for example, the C-V hysteresis curves associated with two different completed CdTe modules after various conditioning exercises. More detail on the latter procedures can be found in Ref.[17].

The greater hysteresis, and movement of the C-V determined \( W_d \) observed in module #X1 correlated with a performance degradation of ~8.3%. For module #X7, module performance decreased ~ 1.0% during test.

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