Direct Analysis of the Current Density vs. Voltage Curves of a CdTe Module during Outdoor Exposure

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Abstract — Current density-voltage (JV) curves of a CdTe photovoltaic module measured during 2.5 years of outdoor operation are analyzed using a phenomenological four-parameter equation. This approach is shown to be more accurate than fitting the same data set to the conventional five parameter diode equation. The four extracted parameters are the short-circuit current density J_{sc} , open-circuit voltage V_{oc} , and the differential resistances R_{sc} and R_{oc} , i.e., the reciprocal slopes of the JV curves at short circuit and open circuit, respectively. The dependencies of all four parameters on module temperature and irradiation intensities are analyzed in terms of physically motivated models. The coefficients derived from these models are then used to transform the photovoltaic parameters to reference conditions and to investigate the degradation of the module. The models for R_{sc} and R_{oc} involve voltage-dependent carrier collection. This feature appears prominent already in the initial JV curves, but becomes even more dominant with increasing exposure time. Voltage-dependent carrier collection also explains that the diode ideality factor determined from V_{oc} vs. J_{sc} curves is different from that determined using R_{oc} vs. $1/J_{sc}$ plots. The degradation of the module is essentially reflected in fill factor losses caused by a decrease of R_{sc} and an increase of R_{oc} . Additionally, the V_{oc} vs. $\log(J_{sc})$ curves of the module behavior at low irradiation unveil an increasing influence of a double-exponential diode behavior.

Keywords — current-voltage characteristic, degradation, monitoring, CdTe, diode ideality factor, reliability.

1. Introduction

In view of a global solar photovoltaic (PV) capacity surpassing the 100 GW milestone [EPIA, 2014], accurate monitoring of the outdoor performance of solar modules or PV systems is of utmost importance. Continuous measurement of complete current density-voltage (JV) curves of modules during outdoor operation yields especially important information on specific technologies. The evaluation of the JV curve data requires the application of specific models, as reviewed recently by Cotfas et al., 2013. Most performance models account for the varying irradiance and module temperature during operation [King et al., 2004; Williams et al., 2005; Guérin de Montgareuil, 2007; Sutterlueti et al., 2011; Merten et al., 2012; Stein et al., 2013]. The coefficients derived by application of the models to the data are used in the analysis of the outdoor degradation, but also, to predict the performance of the module under given irradiation conditions, temperatures, and other conditions. Failure of accurate prediction is an indicator of additional degradation, i.e., a change of the physical module behavior over time of exposure. When considering time intervals shorter than the entire outdoor exposure, specific changes of the module coefficients with time and (changing) dependence on irradiance and temperature can be calculated and the effect of their degradation is quantifiable. The translation of acquired outdoor data to standard conditions [IEC 60891] requires the determination of temperature-correction and curve-correction parameters that are often measured indoors and usually only at the beginning of the exposure [IEC60904]. These coefficients may not hold for the

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entire time of outdoor exposure. Additionally, coefficients determined for many performance models are not physically motivated and the corresponding changes over operation time cannot be interpreted in terms of changing physical device properties.

The present paper introduces a simple four-step procedure to analyze acquired JV data in terms of the underlying physics. In a first step (i), all measured JV curves are fitted with the help of a four-parameter equation [Karmalkar and Haneefa, 2008]. The four independent parameters represent or translate into the short-circuit current density J_{sc} , open-circuit voltage V_{oc} , and differential resistances R_{sc} and R_{oc} (i.e., the reciprocal slopes of the JV curves) at short circuit and open circuit. The use of the Karmalkar-Haneefa (KH) equation allows us to reduce the number of parameters because the fits obtained using only J_{sc} , V_{oc} , R_{sc} , and R_{oc} determine the entire JV curve including the fill factor FF . In step (ii), we analyze the dependence of J_{sc} on module temperature T and irradiation intensities ϕ , as well as the dependencies of the other parameters on T and J_{sc} . This analysis yields physically motivated coefficients for the functional dependence of the four parameters on T and ϕ . A period of one to two weeks with acquisition of JV curves every 15 min is sufficient for a reliable determination of these coefficients. Note that the number of data points is reduced by an applied filtering before determination of the coefficients. Step (iii) uses the model equation and the acquired parameters to calculate the PV output parameters at reference conditions. Finally, in step (iv), the time series of the PV output parameters, as well as that of the time development of the coefficients, is analyzed to investigate the degradation. In the present case, the analysis unveils clear fingerprints of an increasing influence of voltage-dependent carrier collection. Whereas the accuracy of our method is sufficient to analyze the degradation, a correction of the absolute values of the maximum output power is necessary to improve the precision of absolute output power prediction to the usual standard.

2. Experimental Field Data

The investigated CdTe module is a prototype chosen because it shows an unusually high degradation rate, allowing us to better study the signature of degradation. The module consisted of a series connection of 58 cells with a cell area of 8675.4 cm². The module was exposed outdoors on the Performance and Energy Rating Testbed (PERT) at the National Renewable Energy Laboratory (NREL), Golden, CO, USA. The module was mounted at the latitude tilt of 40° ($\pm 1^\circ$) facing south ($\pm 2^\circ$) and was held at maximum power with current-voltage curves taken typically every 15 minutes. Environmental parameters were recorded simultaneously and included plane-of-array (POA) irradiance (Wm⁻², measured by a thermopile), wind speed (m/s), ambient temperature (°C), and back-of-module temperature (°C), as previously detailed by del Cueto (2005). For the analysis, we only used the raw current-voltage IV curve data, as well as the temperature T_{meas} measured at the rear of the module and the POA irradiance ϕ_{meas} . Modules were not cleaned. The irradiance sensor was cleaned weekly. Measurements on a nearby pair of cleaned and uncleaned modules showed that average soiling was < 2%. The related noise is effectively removed during the analysis, as described below.

The data filtering follows the approach published by Jordan and Kurtz (2014). We sorted out data measured under unstable irradiation conditions (irradiance change > 5% between recorded value before and after each trace) and at module temperatures lower than 5°C. Also, curves with unreasonably low or high fill factor FF or $I_{sc,meas}/\phi_{meas}$ values were carefully removed.

A reversible degradation is typical for thin-film devices. CdTe modules are built in p-n configuration. Instead of doped layers of the same material, a CdS layer forms the n-type buffer for a CdTe p-layer. The

Ohmic contact metallization is deposited last. Sometimes, a Cu-containing component is included that can cause instabilities [Gostein and Dunn, 2011]. There are several further sources of degradation, for example, trap states [Sasala and Sites, 1993] in the absorber junction, series resistance of the back contact [Carlsson and Brinkman, 2006], and ion migration [Pudov et al., 2002; Jenkins et al., 2003; Corwine et al., 2004]. Light-exposure and bias application can enhance or deteriorate device performance depending on conditions and specific arrangement of the layers, material composition, and the back contact [Carlsson and Brinkman, 2006; del Cueto and von Roedern, 2006; Hegedus and McCandless, 2005] in CdTe modules. It is impossible to distinguish between those degradation mechanisms looking at the JV data alone. Yet, the JV data enable us to investigate the signature of these degradation mechanisms. In the following, we show how such signatures are distilled out of the JV data acquired during outdoor exposure.

3. Analysis Method

In 2008, Karmalkar and Haneefa proposed a phenomenological equation for evaluating illuminated JV curves of solar cells according to

$$J(V) = J_{sc} \left[(1 - \gamma) \frac{V}{V_{oc}} + \gamma \left(\frac{V}{V_{oc}} \right)^m - 1 \right]. \quad (1)$$

Compared to the many existing methods to analyze JV curves [Cotfas et al., 2013], Eq. 1 has the advantage that it only depends on four parameters, i.e., short-circuit current density J_{sc} , open-circuit voltage V_{oc} , and the dimensionless quantities γ and m . This equation also has the advantage of being very easy to implement since all four parameters can be directly derived from the curve, then optimized (to reduce the effects of noise or inaccurate initial estimation of the four parameters) quite easily with a regression relative to the power vs. voltage curve. Illuminated current-voltage curves from a wide variety of solar cells can be fitted accurately by this approach. Equation 1 by itself has no physical meaning; but various, more complex, physically motivated solar cell models are compatible with the equation, as shown by Das and Karmalkar (2011).

From Eq. 1, the fill factor FF can be calculated via

$$FF = \frac{V_{mpp}}{V_{oc}} \left\{ 1 - (1 - \gamma) \frac{V_{mpp}}{V_{oc}} - \gamma \left(\frac{V_{mpp}}{V_{oc}} \right)^m \right\}, \quad (2)$$

where the voltage V_{mpp} at the maximum power point is given by [Das and Karmalkar, 2011]

$$\frac{V_{mpp}}{V_{oc}} = (m + 1)^{-1/m} - \left[(m + 1)^{-1/m} - 0.5 \right] (1 - \gamma)^{1.58 + 0.05m} \quad (3)$$

and the current density at the maximum power point $J_{mpp} = J_{mpp}(V_{mpp})$ is obtained by Eq. 1. For the present purpose, we make use of the fact that the validity range of Eq. 1 — namely, the quadrant of energy extraction of the illuminated characteristics — fits to the range of our experimental data. As shown below, Eq. 1 is able to fit the relatively featureless current-voltage curves of PV modules over a wide range of irradiation intensities ϕ and module temperatures T .

Furthermore, the parameters γ and m are directly related to the differential resistances R_{oc} and R_{sc} , respectively, the differential conductances G_{oc} and G_{sc} at the short-circuit (sc) and open-circuit (oc) points of the current-voltage curves via

$$\frac{1}{R_{sc}} = G_{sc} = \left. \frac{dJ}{dV} \right|_{V=0} = \frac{J_{sc}}{V_{oc}} (1 - \gamma) \quad (4)$$

and

$$\frac{1}{R_{oc}} = G_{oc} = \left. \frac{dJ}{dV} \right|_{V=V_{oc}} = \frac{J_{sc}}{V_{oc}} (1 - \gamma + \gamma m) . \quad (5)$$

Inversion of Eqs. 4 and 5 yields

$$\gamma = 1 - G_{sc} \frac{V_{oc}}{J_{sc}} \quad (6)$$

and

$$m = \frac{V_{oc} (G_{oc} - G_{sc})}{J_{sc} - V_{oc} G_{sc}} . \quad (7)$$

We note that the quantities R_{sc} and R_{oc} are not identical to the parallel and series resistance R_p and R_s of the textbook equivalent circuit of a solar cell. However, possible changes in R_{sc} and R_{oc} give an indication of whether a degradation mechanism is more parallel-resistance-like (indicated by changes in R_{sc}) or more series-resistance-like (indicated by changes in R_{oc}). Furthermore, both quantities can be described in terms of physical models, as shown in sections 4.2 and 4.4.

Figures 1a and 1b display various measured and fitted JV curves, along with the graphical definitions of the four parameters (Fig. 1a) used in the KH equation. Note here and in the following that the data are scaled to the current density J per unit cell area and the voltage V per cell. With Eq. 1, we are able to fit the JV curves of PV modules over a wide range of irradiation intensities ϕ_{meas} and temperatures T_{meas} .

Fig. 1. Fit of the Karmalkar-Haneefa (KH) equation to the measured JV curves. a) The KH equation uses four fit parameters: J_{sc} , open-circuit voltage V_{oc} , and differential resistances R_{sc} and R_{oc} , as marked. b) The equation provides very good fits of the JV curves (raw data in black) at various stages in degradation and acquired at various irradiance levels (red lines).

4. Irradiance and Temperature Dependence

As mentioned previously (step (ii) in section 1), we analyze all four parameters J_{sc} , V_{oc} , R_{sc} , and R_{oc} used in the KH equation in terms of their dependencies on module temperature T and irradiance intensities ϕ (J_{sc}) or in terms of their dependencies on module temperature and short-circuit current density J_{sc} (V_{oc} , R_{sc} , R_{oc}).

4.1 Short-Circuit Current Density

The short-circuit current density J_{sc} is proportional to the irradiance intensity ϕ_{meas} , where the proportionality constant depends on the module temperatures T_{meas} according to

$$J_{sc,meas}(\phi_{meas}, T_{meas}) = \{\alpha_{Jsc} T_{meas} + \kappa_{Jsc}\} \phi_{meas}. \quad (8)$$

Knowledge of the coefficients α_{Jsc} and κ_{Jsc} allows one to calculate $J_{sc@ref}$ for any desired reference condition expressed by a reference irradiance ϕ_{ref} and a reference module temperature T_{ref} . Likewise, one may translate the raw values J_{sc} directly to the reference condition using

$$J_{sc@ref} = \{\alpha_{Jsc} (T_{ref} - T_{meas})\} \phi_{ref} + J_{sc,meas}(\phi_{ref} / \phi_{meas}), \quad (9)$$

where the first term accounts for the correction of T_{meas} and the second for the corrections of ϕ_{meas} .

Figure 2 shows the $J_{sc,meas}$ data for a one-week time interval versus measured irradiance ϕ_{meas} (raw data are black dots). The raw data are used to calculate the respective coefficients α_{Jsc} and κ_{Jsc} for temperature and

irradiance dependence. The derivation of these coefficients from outdoor data include the dependence of the module performance on T and ϕ as well as the effects of any systematic variations in spectrum with T or ϕ , including angle-of-incidence effects. This figure shows the result of a temperature correction only, to $T_{\text{ref}} = 40^\circ\text{C}$ (using only the first correction term in Eq. 9, orange triangles in figure). The effect of the temperature T_{meas} is small and the linear dependence of $J_{\text{sc,meas}}$ on ϕ_{meas} remains essentially unchanged. The final values $J_{\text{sc@ref}}$ (blue diamonds) were translated to both reference values $\phi_{\text{ref}} = 1000 \text{ Wm}^{-2}$, $T_{\text{ref}} = 40^\circ\text{C}$. The data above $\phi_{\text{meas}} = 500 \text{ Wm}^{-2}$ show no irradiance dependence after this correction, whereas some scatter of values is observed in the low irradiance range. Note that week 1 is not the first week of outdoor exposure. Some tests were performed indoors and outdoors prior to the long-term data acquisition.

Fig. 2. Translation of short-circuit current density $J_{\text{sc,meas}}$. Data from outdoor-measured JV curves are translated to reference conditions $\phi_{\text{ref}} = 1000 \text{ Wm}^{-2}$, $T_{\text{ref}} = 40^\circ\text{C}$ shown as a function of measured irradiance ϕ_{meas} for week 1. Raw data (black dots) are translated to $J_{\text{sc@ref}}$ at reference module temperature T_{ref} (orange triangles) and reference irradiation intensity ϕ_{ref} (blue diamonds).

Figure 3 shows the short-circuit current density $J_{\text{sc@ref}}$ translated to reference conditions based on a weekly data analysis. $J_{\text{sc@ref}}$ shows a slight seasonal variation, but no apparent degradation over the 2.5-year time period. The seasonal variation roughly follows the variation in average photon energy (APE) [Jardine et al., 2002], i.e., the variations of the ratio between blue and red photons in the incident spectrum compared to the AM1.5g spectrum. Because no measurements of the local spectrum were acquired at the time of the experiment, a correction of the data for spectral variations is not considered in the following.

Fig. 3. Short-circuit current density $J_{\text{sc@ref}}$ (black dots) translated to reference module temperature $T_{\text{ref}} = 40^\circ\text{C}$ and reference irradiation intensity $\phi_{\text{ref}} = 1000 \text{ Wm}^{-2}$. Except for a small seasonal variation, the

data show no significant degradation. A linear fit to the data (black line) has a slope of $-0.02(\pm 0.04)$ $\text{mAcm}^2/\text{year}$, i.e., the degradation is below the error limit.

Linear fits are added to Figs. 5a), 5b), 7, 9a), 9b), and 12 (black lines), as done here in Fig. 3. Note also that in the following, we have replaced the dependence on ϕ_{meas} by a dependence on $J_{\text{sc,meas}}$. This replacement is justified by the linear interdependence of both quantities, shown for the first week of data in Fig. 2. The slope of this linearity changes little following the seasonal irradiation changes over time of outdoor exposure (not shown). As a reference value, we replace $\phi_{\text{ref}} = 1000 \text{ Wm}^{-2}$ by $J_{\text{sc,ref}} = 19.3 \text{ mAcm}^{-2}$, the value of $J_{\text{sc@ref}}$ in the first week. By substituting ϕ_{meas} by $J_{\text{sc,meas}}$, we eliminate those effects of fluctuations due to the seasonal spectral changes. Annealing and degradation due to temperature and illumination exposure are still reflected by the data. This replacement, following the self-irradiance approach as suggested by King et al., (2004), reduces the scatter in the analysis of the outdoor data.

4.2 Differential conductance at short circuit

In an ideal solar cell, one would not expect a dependence of the conductance $G_{\text{sc,meas}}$, or the resistance $R_{\text{sc,meas}}$, on either T_{meas} or $J_{\text{sc,meas}}$. However, the outdoor data (as shown in Figs. 4a) and b)) point to a distinct direction. Here, we find a pronounced dependence on both external parameters that is well described by a linear dependence on T_{meas} and $J_{\text{sc,meas}}$

$$G_{\text{sc,meas}}(J_{\text{sc,meas}}, T_{\text{meas}}) = G_{\text{sc,0}} + \alpha_{\text{Gsc}} T_{\text{meas}} + \kappa_{\text{Gsc}} J_{\text{sc,meas}}. \quad (10)$$

Using Eq. 10, we obtain the translation equation

$$G_{\text{sc@ref}} = G_{\text{sc,meas}} + \alpha_{\text{Jsc}} (T_{\text{ref}} - T_{\text{meas}}) + \kappa_{\text{Jsc}} (J_{\text{sc,ref}} - J_{\text{sc,meas}}). \quad (11)$$

Note that the strong dependence of the differential resistance G_{sc} on J_{sc} can be explained by voltage-dependent photocurrent collection (Hegedus et al., 2007), where the photocurrent at a given junction voltage is given by $J_{\text{ph}}(V_j) = J_{\text{ph}}^{\text{max}} f(V_j)$, where $f(V_j)$ is the collection efficiency or collection function. The coefficient κ_{Gsc} is then given by $\kappa_{\text{Gsc}} = df/dV_j / f$. Note that an illumination-dependent shunt resistance could have the same effect, which would lead to an expression that is mathematically equivalent to Eq. (10) because of the linear dependence of $J_{\text{sc,meas}}$ on ϕ_{meas} (cf. Fig. 2). Furthermore, solar cells—and especially solar modules with a spatially inhomogeneous distribution of series and shunt resistances—may also exhibit such bias-dependent shunting behavior (see, e.g., Breitenstein, 2013, as well as Bowden and Rohatgi, 2001).

Figure 4 presents the raw data of the conductance at short-circuit $G_{\text{sc,meas}}$ extracted from the JV curves of one week of outdoor exposure (black dots) for week 1 (Fig. 4a) and week 106 (Fig 4b). Note the change of scale between (a) and (b), reflecting the increase of $G_{\text{sc@ref}}$ during exposure time. The temperature correction alone (orange triangles) has only a weak influence in the low-temperature/low-irradiance range and little consequence in the high-temperature/high-irradiance range. Translation to T_{ref} and $J_{\text{sc,ref}} = 19.3 \text{ mAcm}^{-2}$ results in the blue open diamonds. The curvature in the translated data $G_{\text{sc@Tref,Jsc,ref}}$ (open diamonds) in Fig. 4a) indicates that the simple linear dependence of G_{sc} on $J_{\text{sc,meas}}$ is not perfectly accurate. However, restriction of the range of analysis to higher values of $J_{\text{sc,meas}}$ ($15 \text{ mAcm}^{-2} \cdot J_{\text{sc,meas}} \cdot 25 \text{ mAcm}^{-2}$) yields a flat distribution of the translated data (blue full diamonds). Regardless of the fitting range, the major effect of bias-dependent current collection is accounted for by the use of Eqs. 10 and 11, especially when comparing the data in the early state (Fig. 4a), week 1, $G_{\text{sc@ref}} \cdot 2.3 \text{ mScm}^{-2}$) with a later state of exposure (Fig. 4b), week 106, $G_{\text{sc@ref}} \cdot 5.5 \text{ mScm}^{-2}$).

Fig. 4. Translation of differential conductance $G_{sc,meas}$ from outdoor-measured JV curves to reference conditions for week 1 (a) and week 106 (b). The raw data $G_{sc,meas}$ (black dots) are translated to the reference temperature $T_{ref}=40^{\circ}\text{C}$ (full triangles), and additionally current density $J_{sc,ref}=19.3\text{ mAcm}^{-2}$ (open diamonds) according to Eq. (11). Restricting the fitting range to current densities $15\text{ mAcm}^{-2} \leq J_{sc,meas} \leq 25\text{ mAcm}^{-2}$ yields a flatter distribution of the corrected data (full diamonds).

Figure 5 depicts the coefficients obtained from fitting Eq. (10) to the weekly data intervals together with the value $G_{sc@ref}$ (black squares) translated to reference conditions. Note that here and in the Figs. 7, 9, 10, 11, and 12, the given data have been calculated using the restricted fitting range of short-circuit current densities $15\text{ mAcm}^{-2} \leq J_{sc,meas} \leq 25\text{ mAcm}^{-2}$. In Fig. 5a), the coefficient for the temperature correction α_{Gsc} and the extrapolated shunt conductance $G_{sc,0}$ have been combined to $G_{sc,0@Tref} = G_{sc,0} + \alpha_{Gsc}T_{ref}$ (gray squares), i.e., the shunt conductance at reference temperature. Figure 5b) gives the coefficient for current correction κ_{Gsc} . All values increase over time. The annual degradation of $G_{sc,0@Tref}$ ($0.62\text{ mScm}^{-2}/\text{year}$) and that of κ_{Gsc} multiplied by J_{ref} ($0.68\text{ mScm}^{-2}/\text{year}$) add up to the degradation of $G_{sc@ref}$ ($1.3\text{ mScm}^{-2}/\text{year}$). Thus, the overall increase of $G_{sc@ref}$ is caused equally by the increase of the irradiance-independent shunt resistance and by the increasing influence of bias-dependent photocurrent collection. The latter effect is negligible at the beginning of the exposure, with κ_{Gsc} being close to zero, but becomes more prominent during time of exposure, as already demonstrated by the data in Figs. 4a) and 4b).

Fig. 5. Translation coefficients for G_{sc} . Coefficients $G_{sc,0@Tref}$ (gray squares in a), κ_{Gsc} (b) gained from fitting the experimental data to Eq. (10) on a weekly basis, as well as the differential resistance $G_{sc@ref}$ (black squares in a) translated to the reference conditions $T_{ref} = 40^\circ\text{C}$ and $J_{sc,ref} = 19.3 \text{ mAcm}^{-2}$ via Eq. (11).

4.3 Open-circuit voltage

The dependence of the open-circuit voltage $V_{oc,meas}$ on T_{meas} and $J_{sc,meas}$ follows from the standard diode equation of an illuminated solar cell [Nelson, 2003]

$$V_{oc} = E_a / q - nkT / q \log(J_{00}) + nkT / q \log(J_{sc}). \quad (12)$$

Thus, we use the equation

$$V_{oc,meas}(J_{sc,meas}, T_{meas}) = V_{oc}^0 - \{\alpha_{Voc} - \epsilon_{Voc} \log(J_{sc,meas})\} T_{meas}. \quad (13)$$

The correction toward reference conditions is obtained via

$$\begin{aligned} V_{oc@ref} &= V_{oc,meas}(J_{sc,ref}, T_{ref}) = V_{oc}^0 - \alpha_{Voc} T_{ref} + \epsilon_{Voc} T_{ref} \log(J_{sc,ref}) \\ &= V_{oc,meas} - \{\alpha_{Voc} - \epsilon_{Voc} \log(J_{sc,meas})\} (T_{ref} - T_{meas}) \\ &\quad + \epsilon_{Voc} T_{ref} \log(J_{sc,ref} / J_{sc,meas}) \end{aligned} \quad (14)$$

allowing again for the separate correction for T_{meas} and $J_{sc,meas}$.

Figures 6a) and 6b) show the raw V_{oc} data (black dots) and data translated to T_{ref} (orange full triangles) for week 1 and 106, respectively. After elimination of the temperature dependence, the $V_{oc}[\log(J_{sc})]$ relationship shows the linear (logarithmic) dependence expected from Eq. 13 (blue open diamonds). Also

shown in the data is the fact that at low current densities, the slope of the semi-logarithmic plots (especially in Fig. 6b) is larger than in the range of large current densities. Such a “double-exponential” or “double-logarithmic” behavior (of the V_{oc} vs. $\log(J_{sc})$ relationship) is known for most solar cells (see, e.g., Wolf et al., 1977). This behavior is due to different dominant recombination mechanisms at high and low bias. The diode ideality factor analyzed for current densities between 15 and 25 mAcm^{-2} is slightly above unity, whereas the ideality factor analyzed for current densities between 4 and 7.4 mAcm^{-2} is in the range of 3.5–4.5. Such high ideality factors at low to moderate forward bias have been previously observed in early days of PV research (see, e.g., Queisser, 1962). A comprehensive review of different mechanisms leading to ideality factors larger than two was recently given by Breitenstein (2013). Note that models for double-exponential behavior in the classical sense are one-dimensional models. However, spatially extended models (considering networks of resistors and diodes) also predict double-exponential behavior, including unusually high diode ideality factors [Grabitz et al., 2005; Breitenstein, 2013; Breitenstein and Rissland, 2013]. Thus, we must keep in mind that although most of our discussion is conducted in terms of simple one-dimensional models, the spatially extended, inhomogeneous nature of the module might offer different explanations.

Because of the double-exponential behavior, Eqs. (13) and (14) must be applied separately to different J_{sc} ranges. At the beginning of exposure (Fig. 6a), the secondary diode is not very pronounced. Consequently, a translation of the measured values $V_{oc,meas}$ to the standard conditions T_{ref} and $J_{sc,ref}$ leads to constant values $V_{oc@ref}$ in the entire range of short-circuit current densities (open blue diamonds). With increasing exposure time, the secondary diode becomes more pronounced (bending in Fig. 6b). Therefore, application of a single diode model for all values $J_{sc,meas}$, instead of yielding constant values, leads to a considerable bending of $V_{oc@ref}$ (open diamonds). In contrast, restriction of the fitting range to high bias conditions of 15 $\text{mAcm}^{-2} \leq J_{sc,meas} \leq 25 \text{ mAcm}^{-2}$ leads to constant values for $V_{oc@ref}$ (full diamonds). Thus, a self-consistent transformation of the measured values is only feasible under restriction to bias conditions where the data correspond to a single diode, either the primary or secondary one.

Fig. 6. Translation of open-circuit voltage $V_{oc,meas}$ from outdoor-measured JV curves to reference conditions ($T_{ref} = 40^\circ\text{C}$ and $J_{sc,ref} = 19.3 \text{ mAcm}^{-2}$) for a) week 1 and b) week 106. The $V_{oc,meas}$ data extracted from the measured JV curves (black dots) are translated to reference temperature T_{ref} (full triangles) and current

density $J_{sc,ref}$ (open diamonds). Restricting the fitting range to current densities $15 \text{ mAcm}^{-2} \leq J_{sc,meas} \leq 25 \text{ mAcm}^{-2}$ yields a flatter distribution of the corrected data (full diamonds).

Figure 7 depicts the temporal change in the correction coefficients α_{Voc} (gray open squares), ϵ_{Voc} (red open squares), and $V_{oc,0}$ (green full circles) and of the calculated voltage at reference conditions $V_{oc@ref}$ (full squares). A significant decrease of $V_{oc@ref}$ by about 20 mV within the time of exposure is observed. A linear fit to the time series $V_{oc@ref}(t)$ yields an average decline of 9.2 mV/year (per cell), whereas the linear fits show increases and decreases by about the same amount in $\epsilon_{Voc}(t) \times 313 \text{ K} \times \log(19.3[\text{mAcm}^{-2}])$, $V_{oc,0}$ and $\alpha_{Voc} \times 313 \text{ K}$. The sum results in the decline of $V_{oc@ref}$.

Fig. 7. Time evolution of $V_{oc@ref}$ and of the translation coefficients in Eq. (13) and Eq. (12). The linear fits to the coefficients α_{Voc} (gray open squares), $V_{oc,0}$ (green dots), and ϵ_{Voc} (red open squares) show that the contributions add up to the degradation of $V_{oc@ref}$ (black dots) by almost equal shares. $V_{oc@ref}$ degrades by about $9.2(\pm 0.7) \text{ mV/year}$.

4.4 Differential resistance at open circuit

The differential resistance R_{oc} at open circuit is a series connection of the diode resistance and a linear series resistance R_s according to

$$R_{oc,meas}(J_{sc,meas}, T_{meas}) = R_s + \beta_{Roc} T_{meas} / J_{sc,meas} + \alpha_{Roc} T_{meas}. \quad (15)$$

Note for the diode resistance that the coefficient β_{Roc} in a single-diode model corresponds to nk/q , where k denotes Boltzmann's constant, q the elementary charge, and n the diode ideality factor. The equation used corresponds to Eq. 9 in Werner (1988). The correction function resulting from Eq. 15 finally reads

$$R_{oc@ref} = R_{oc,meas} - \beta_{Roc} (T_{meas} / J_{sc,meas} - T_{ref} / J_{sc,ref}) - \alpha_{Roc} (T_{meas} - T_{ref}). \quad (16)$$

Fig. 8. Translation of open-circuit resistance R_{oc} from outdoor-measured JV curves to reference condition. a) Week 1, b) week 106, R_{oc} extracted from the measured JV curves (black dots) is translated to reference temperature T_{ref} (orange full triangles). The translation to both temperature T_{ref} and irradiance/current $J_{sc,ref}$ conditions (open diamonds) results in an almost straight line. Restricting the fitting range to current densities $15 \text{ mAcm}^{-2} \leq J_{sc,meas} \leq 25 \text{ mAcm}^{-2}$ yields a flatter distribution of the corrected data (full diamonds), as also highlighted in the insets in a) and b) that zoom into the high current-density range of the same data.

Fig. 9. Time evolution of $R_{oc@ref}$ ($T_{ref} = 40^\circ\text{C}$, $J_{sc,ref} = 19.3 \text{ mAcm}^{-2}$) and of the translation coefficients. $R_{s@Tref}$ (gray squares in a) and β_{Roc} (b) are gained from fitting the experimental data to Eq. (15) on a weekly basis. The linear fit to $R_{s@ref}$ reveals a decrease of $0.5 \Omega\text{cm}^2/\text{year}$, β_{Roc} increases by 0.05 mV/K/year . The latter corresponds to an increase by $0.9 \Omega\text{cm}^2/\text{year}$, which adds up and is consistent with the increase in $R_{oc@ref}$ (black squares) of $0.5 \Omega\text{cm}^2/\text{year}$.

Figures 8a) and 8b) display experimental R_{oc} data gained at different times of outdoor exposure: week 1 (Fig. 8a) and week 106 (Fig. 8b). The raw data (black dots) exhibit a drastic increase during those two years of outdoor operation. Temperature correction transforms the measured values $R_{oc,meas}$ to $R_{oc@Tref}$ (orange triangles) with only little change. At the beginning of exposure, the plot $R_{oc@Tref}$ vs. $1/J_{sc}$ (Fig. 8a) yields approximately a straight line—as expected from the single-diode law underlying Eq. (15) whereas the corresponding data in Fig. 8b) exhibit two different slopes under high-bias and low-bias conditions. This finding is in agreement with the double-logarithmic feature found in the V_{oc} vs. $\log(J_{sc})$. Consequently, the final correction for both, temperature and current density, yields a clear bending in the data (open diamonds). Only restriction of the fitting range $15 \text{ mAcm}^{-2} \leq J_{sc,meas} \leq 25 \text{ mAcm}^{-2}$ (full diamonds), also highlighted in the inset, yields a flat distribution of the corrected data.

Figure 9a) displays the time evolution of the differential resistance $R_{oc@ref}$ (black squares), which shows a considerable increase of $0.5 \Omega\text{cm}^2/\text{year}$. The Ohmic series resistance $R_{s@Tref} = R_s + \alpha_{Roc} T_{ref}$ (gray squares) at reference temperature is relatively small (around $1\text{--}2 \Omega\text{cm}^2$ as compared to $6\text{--}7 \Omega\text{cm}^2$ for $R_{oc@ref}$). Because of Eq. (15), the increase of $R_{oc@ref}$ is defined by the sum of the decrease of $R_{s@Tref}$ by $0.5 \Omega\text{cm}^2/\text{year}$ and the annual increase of β_{Roc} by $0.055 \text{ mV/K} \times 313 \text{ K} / 19.3 \text{ mAcm}^{-2} = 0.9 \Omega\text{cm}^2$. Note that the increase of β_{Roc} is

equivalent to an increase of the diode ideality factor n . This observation will be more closely discussed in sect. 5.2.

5. Time Evolution of Photovoltaic Parameters

5.1 Degradation at standard conditions

Up to this point, we have analyzed the four parameters of the KH equation individually with the help of the time evolution of physically motivated coefficients. The physical meaning of the four parameters opens up the opportunity to interpret the physics behind the degradation. This is not possible for most existing methods where the parameters relate to quantities that cannot directly be interpreted (as e.g. the FF). Because the fill factor depends on R_{sc} and R_{oc} via Eq. (2), we are now able to reconstruct the time evolution of the complete set of PV parameters from our results above. Figure 10 shows the time evolution of short-circuit current density $J_{sc@ref}$, open-circuit voltage $V_{oc@ref}$, and the power $P_{mpp@ref}$, and fill factor $FF_{@ref}$ calculated from the JV curves translated to reference conditions. The $FF_{@ref}$ and $P_{mpp@ref}$ data were corrected after Eq. A.2. As stated earlier, $J_{sc@ref}$ fluctuates with seasonal spectral changes but without significant degradation ($< 0.1\%/year$) and $V_{oc@ref}$ decreases by a rate of 9.2 mV (1.3%) per year. However, the major influence on the degradation of the output power (5.8%/year) stems from the degradation of the $FF_{@ref}$ (4.5%/year).

Fig. 10. Time evolution of the normalized PV parameters at standard reference conditions ($T_{ref} = 40^\circ\text{C}$, $\phi_{ref} = 1000 \text{ Wm}^{-2}$). A degradation of the seasonally fluctuating short-circuit current density $J_{sc@ref}$ (black dots) is not significant ($< 0.1 \text{ \%/year}$). The open-circuit voltage $V_{oc@ref}$ (orange triangles) degrades by about 1.3% per year. The degradation of the fill factor $FF_{@ref}$ (red circles) by about 4.5% per year yields the largest contribution to the degradation of the maximum power output $P_{mpp@ref}$ (5.8%/year, blue diamonds).

The dependence of the fill factor $FF_{@ref}$ on $R_{oc@ref}$ and $R_{sc@ref}$ enables us to determine how much of the degradation is due to changes in each parameter. Figure 11 displays the original calculated fill factor data $FF_{@ref}$ normalized to the start value at week 1 (black dots, same data as in Fig. 10). All data were corrected as explained in A.1. Also shown are two sets of reconstructed $FF_{@ref}$ data with the respective influence of $R_{oc@ref}$ and $R_{sc@ref}$ degradation removed. The difference from the original data to the data with $R_{oc@ref}$ degradation removed is slightly larger than the difference from the data with $R_{sc@ref}$ degradation removed. This finding points to an influence of $R_{sc@ref}$ degradation on $FF_{@ref}$ degradation that is slightly larger than that

of $R_{oc@ref}$ degradation. However, because both $R_{oc@ref}$ and $R_{sc@ref}$ degradation essentially result from the increasing influence of bias-dependent carrier collection, this mechanism is also the main source of the overall $FF_{@ref}$ degradation.

Fig. 11. Origin of fill factor degradation. The fill factor $FF_{@ref}$ drop of the JV curves was calculated via Eq. (2) and normalized to compare the influence of degradation in $R_{sc@ref}$ and $R_{oc@ref}$ combined (original data, black dots), only in $R_{sc@ref}$ (purple full triangles), respectively, $R_{oc@ref}$ (orange open triangles), and no degradation in the two (gray stars). $R_{sc@ref}$ degradation dominates the $FF_{@ref}$ degradation slightly. Assuming no degradation in $R_{oc@ref}$ and $R_{sc@ref}$, only a loss $< 1\%$ remains of the 10.6% total $FF_{@ref}$ loss after 2.5 years of outdoor exposure.

5.2 Influence of voltage-dependent photocurrent collection on the ideality factor

The diode ideality factor n can be calculated from the available data in two ways: from Eq. 12 (corresponding to a plot of V_{oc} vs. $\log(J_{sc})$, cf. Fig. 6), and from Eq. 16 (corresponding to a plot of R_{oc} vs. $1/J_{sc}$, cf. Fig. 8). For a simple single-diode model, both methods should yield the same result. As shown in appendix A.2, the voltage-bias dependence of the photocurrent affects the V_{oc} vs. $\log(J_{sc})$ and the R_{sc} vs. $1/J_{sc}$ relationship in different ways: The V_{oc} vs. $\log(J_{sc})$ method yields ideality factors n_{Voc} that are lower than those of the single-diode model, as already shown by Eron and Rothwarf (1984). In contrast, the ideality factor n_{Roc} obtained from the R_{sc} vs. $1/J_{sc}$ method substantially overestimates the ideality factor. Thus, a systematic discrepancy between the results of both methods represents a clear indication of voltage-dependent carrier collection. Figure 12 compares the ideality factors determined by the two different methods. Note that this analysis is based on data under high irradiation conditions with corresponding short-circuit current densities $15 \text{ mAcm}^{-2} \cdot J_{sc,meas} \cdot 25 \text{ mAcm}^{-2}$ to minimize the influence of the secondary diode on both results. Figure 12 demonstrates that n_{Roc} exceeds n_{Voc} by a factor of 3–4 over the entire time of the experiment. Additionally, it is seen that the ideality factor n_{Roc} increases by about 0.6 per year (from a linear fit) as compared to an increase of 0.13 for n_{Voc} . These findings highlight the influence of bias-dependent carrier collection on the overall device behavior, as well as on the degradation of the module. We conclude further that the increase of the coefficient β_{Roc} and of the differential resistance $R_{oc@ref}$ found in section 4.4. also result from the increasing influence of bias-dependent photocurrent collection. This mechanism is consequently the main source of the module degradation.

Fig. 12. Determination of the ideality factor n . Comparison of the ideality factors determined from the temperature-corrected data via the R_{oc} vs. $1/J_{sc}$ method (n_{Roc} , blue dots) and via the V_{oc} vs. $\log(J_{sc})$ method (n_{Voc} , orange triangles). The ideality factor from R_{oc} vs. $1/J_{sc}$ exhibits an increase of 0.6/year (compared to 0.13/year for n_{Voc}), indicating the increasing influence of bias-dependent current collection. The database for the analysis is restricted to short-circuit current densities $15 \text{ mAcm}^{-2} \leq J_{sc, meas} \leq 25 \text{ mAcm}^{-2}$.

6. Model Comparison

The focus of the present work is on the *analysis* of the degradation behavior of the CdTe module. However, based on the present analysis a prediction is also possible for the output power of the module at a given irradiance and module temperature. The following sketches some differences between our approach and established PV performance models from the literature [Sutterlueti et al. 2009, de Soto et al., 2006, Merten et al. 1998].

PV performance models are intended to describe the dependence on the maximum output power $P_{mpp} = P_{mpp}(\phi, T, \dots)$ as a function of irradiance intensity ϕ , module temperature T , and possibly further variables characterizing the incident spectrum, like the average photon energy [Jardine et al., 2002]. Often these performance models fulfill a second scope, namely to *analyze* the behavior of $P_{mpp}(\phi, T, \dots)$ in terms of parameters that are gained from the *JV* characteristics of a module or a system. This is either obtained by fitting of the entire *JV* characteristic to specific equation $J = J[V, p_1, p_2, \dots]$ with a number $i = 1, \dots, N$ of parameters, as in the present case as well as in typical diode models [de Soto et al., 2006], or by extracting the parameters only at characteristic points of the curves (e.g., the Loss Factors Model, LFM [Sutterlueti et al., 2009]). In *fitting models* the functional dependence $P_{mpp} = P_{mpp}(\phi, T, \dots)$ is indirectly obtained by re-evaluation of *JV* curves. In the LFM the output power is a simple product of normalized parameters, a reference value, and correction functions for ϕ and T . Therefore, the LFM might be denoted as a *factorization model*.

In all models, the number N of extracted parameters represents a compromise between the requirement for precision in predicting the performance on the one side and the requirement for a physical meaningful analysis on the other side. For the former purpose, a higher number N increases the precision whereas for a physically meaningful analysis the number of independent parameters should be restricted to those parameters that have a significant dependence on the external variables such that one can describe the parameters with the help of dependencies $p_i(\phi, T, \dots) = p_i(\phi, T, \dots, c_\tau^i, c_\phi^i, \dots)$ yielding a set of coefficients $(c_\tau^i, c_\phi^i, \dots)$

for each parameter. The LFM contains $N = 6$ and the dependence of each parameter on ϕ is described by three coefficients. The T dependence of J_{sc} and V_{oc} in the LFM is linear whereas the other four parameters are assumed to be temperature independent. Single diode models use typically $N = 5$, and in the present work we have restricted ourselves to $N = 4$. This restriction allows us to put more emphasis on the specific analysis of the parameters. For instance, the dependence of R_{sc} on ϕ or the discrepancy between ideality factors determined by different methods are unveiled by the present approach but are not covered by other approaches.

Finally all models predict the output power by its dependence on the parameters, i.e. $P_{mpp} = P_{mpp}(p_1(\phi, T, \dots, c_T^1, c_\phi^1, \dots), \dots)$. In *fitting models* the maximum output power is not a parameter (as it is in the LFM) but has to be recalculated from the JV parameters using the fitting equation. Because of this fact and due to the restricted number of parameters, fitting models can introduce systematic errors. As shown in appendix A1, a systematic error of appr. -0.3% at 30 Wm^{-2} and $+1.0\%$ at 100 Wm^{-2} is introduced by the reconstruction of the JV curves with the KH equation. Note that our degradation analysis (Figs. 10 and 11) is only marginally affected by this error because all values at all times and all temperatures are subject to the same error. However, a correction is required for the purpose of output power prediction. A simple correction function reduces the error to approx. $\pm 0.1\%$ which is comparable to standard deviations in the predictions of other models (Stein et al., 2013). In contrast, the single diode model [de Soto et al., 2006], though having 5 parameters compared to the 4 four parameters of the KH equation, introduces a larger systematic error of 3% and a larger standard deviation of $xx\%$ compared to the KH equation for the present data set. As shown in Appendix A.1 our correction procedure can eliminate the systematic error also for the diode model. However, the standard deviation after correction is still four times larger than for the corrected data based on the KH equation.

7. Conclusions

The application of the four-parameter Karmalkar-Haneefa (KH) equation enables one to narrow down the analysis of outdoor-acquired JV data to a minimum set of four parameters. Appendix A1 shows that this fitting is much more accurate than fitting the same data set to a five parameter diode equation [de Soto et al., 2006]. For the subsequent degradation analysis, the dependence of each of the four parameters on irradiation intensity and module temperature (J_{sc}) or on short-circuit current density and module temperature (R_{sc} , V_{oc} , and R_{oc}) is described by standard device-physics models and instead of norm IEC60891 used to translate the data to standard conditions. The dependence of the model coefficients on outdoor exposure time allows one to identify mechanisms underlying the time evolution of the parameters J_{sc} , R_{sc} , V_{oc} , and R_{oc} at reference conditions. Because the fill factor is determined unambiguously by the four parameters, we can also reconstruct on the same basis the time evolution of the output power and the efficiency of the module, thereby discriminating the specific effects of the individual parameters and their coefficients. The accuracy of this prediction is increased by a simple linear correction where the coefficients are extracted directly from the raw data. For the case of the present CdTe module, we have shown that a mechanism with the same indicators as bias-dependent current collection has a major influence on the differential resistances R_{sc} and R_{oc} at short and open circuit. This mechanism is observable at the beginning of outdoor exposure, but also dominates the degradation behavior. This is demonstrated by the fact that the degradation of R_{sc} and R_{oc} , which causes the degradation of the fill factor, is dominated by the same mechanism. Finally, we must keep in mind that effects arising from the spatially distributed nature of a solar module with large areas connected in parallel and many cells connected in series will certainly impact the behavior of the analyzed

parameters. Therefore, we expect that future analyses based on spatially resolved models for thin-film modules will offer refined explanations for some of the observed features.

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Appendix

A.1.

The approximation by the KH equation fit the experimental data over a wide range of irradiances and temperatures reasonably well. However, it is advisable to investigate the error introduced into the reconstruction of the maximum power P_{mpp} by reducing the number of parameters to four. Figure A.1a) plots the ratio $P_{\text{mpp,raw}}/P_{\text{mpp,fit}}$ of raw data to the data reconstructed from the KH equation as the function $P_{\text{mpp,fit}}$. The values of $P_{\text{mpp,raw}}/P_{\text{mpp,fit}}$ lie in a range of ca. + 1.0 and - 0.5 %. A further reduction of this error is achieved by considering the linear relationship

$$\frac{P_{\text{mpp,raw}}}{P_{\text{mpp,fit}}} = a + bP_{\text{mpp,fit}} \quad (A1)$$

valid in the range $30 \text{ W/m}^2 < P_{\text{mpp,fit}} < 90 \text{ W/m}^2$ (Fig. A1). It is important to mention that this relationship is independent of exposure time and only implicitly dependent on irradiation intensity and module temperature. Thus, we can fit the entire data set by Eq. (A1) to obtain $a = 0.9927$ and $b = 0.017 \text{ m}^2/\text{W}$. In turn, the use of the correction equation

$$P_{\text{mpp,corr}} = aP_{\text{mpp,fit}} + bP_{\text{mpp,fit}}^2 \quad (A2)$$

allows us to correct the reconstructed data and finally to reduce the root mean square standard deviation to $\pm 0.085\%$ (Fig. A1). Thus, we can maintain the convenience to reduce the JV-curves to four parameters with their dependence on irradiation intensity and module temperature and at the same time increase the accuracy of our prediction by a simple implicit correction.

To compare the systematic errors due to curve fitting between the KH equation and the single diode equation [de Soto et al., 2006] we fitted our entire data set also to

$$J = J_0 \left[\exp \left(\frac{q(V - JR_s)}{n_{id}kT} \right) - 1 \right] + R_p(V - JR_s), \quad (A3)$$

where J_0 denotes the diode saturation current density, R_s the series resistance, and R_p the parallel resistance. Figure A1 b) demonstrates that the reconstructed maximum output power $P_{\text{mpp,fit}}$ differs by about 3 % (average value of $P_{\text{mpp,raw}}/P_{\text{mpp,fit}}$ is 97.13 % for a range $30 \text{ W/m}^2 < P_{\text{mpp,fit}} < 90 \text{ W/m}^2$) due to the difficulties in modeling the shape of the curve. Obviously, the diode equation does not fit well the low-fill factor data of this thin-film CdTe module and the deviations between measured power and modeled power are significant. This systematic error is removed when applying the correction given by Eq. (A2). However, the great scatter in the data leads to a standard deviation of 0.329 % which is about four times larger than the standard deviation of 0.085 % resulting from the use of the KH equation. Thus, for the present module the use of the KH equation is more suitable for an accurate representation of the measured data than the conventional single diode equation.

Fig. A1. Quotient of the power densities $P_{mpp,raw}$ and $P_{mpp,fit}$ of the raw and the fitted data (triangles). The data is color-coded for time (from red turning to yellow, green, and blue with increasing exposure time). a) The systematic error in the primary fit data (KH equation) is fitted linearly (solid line, Eq. (A1)) and the coefficients of the fits are used to gain the corrected data (red circles) via Eq. (A2) with a standard deviation of 0.085 % (dashed lines). b) Quotient of the power densities $P_{mpp,raw}/P_{mpp,fit}$ for JV curves reconstructed by the single diode equation. The large systematic deviation of 3 % is removed by the correction via Eq. (A2) whereas the remaining standard deviation amounts to 0.329 %, i.e., 3.88 times more than for the reconstruction via the KH equation. Note the difference in scale between a) and b).

A 2.

Voltage-bias dependent collection influences the value of V_{oc} and the slope R_{oc} in different ways. Therefore, the determination of the diode ideality factor n via the $V_{oc}(\log(J_{sc}))$ and via the $R_{oc}(1/J_{sc})$ relationship leads to different results.

Let us describe the JV characteristics by its linear dependence of the current-collection function f on the junction voltage V_j by

$$J_{ph} = J_{ph}^{\max} f(V_j) = J_{ph}^{\max} [f_{sc} + \Delta f - \chi(V - JR_s)] \quad . \quad (A4)$$

Here, J_{ph}^{max} is the maximum photo-generated current density (at $f = 1$), f_{sc} is the value of the collection function at short circuit, $f_{sc} + \Delta f$ is the extrapolated value (see Fig. A2), and $\chi = df / dV_j$ is the slope of the collection function at $V_j = V_{oc}$.

Fig. A2. *JV characteristics (dash dotted line) described by its linear dependence on the current collection function f on the junction voltage V_j . $J_{ph}(V_j) = f(V_j)J_{ph}^{max}$ according to Eq. A1 (black line). The term f_{sc} gives the value of the current-collection function at short-circuit conditions J_{sc} , $f_{sc} + \Delta f$ is the extrapolated value (red dashed line), and $\chi = df / dV_j$ is the slope of the collection function at $V_j = V_{oc}$ (black dashed line marks V_{oc}).*

Combining Eq. A4 with a conventional diode model yields

$$\begin{aligned}
 J &= J_{ph}^{max} [f_{sc} + \Delta f - \chi(V - JR_s)] - J_{00} \exp\left(\frac{-E_a + q(V - JR_s)}{nkT}\right) \\
 &= J_{sc} \left[1 + \frac{\Delta f}{f_{sc}} - \frac{\chi}{f_{sc}}(V - JR_s)\right] - J_{00} \exp\left(\frac{-E_a + q(V - JR_s)}{nkT}\right), \tag{A5}
 \end{aligned}$$

where the junction voltage $V_j = V - JR_s$ is calculated from the externally applied voltage V . At open circuit, it follows from Eq. A5

$$J_{sc} = J_{00} \frac{\exp\left(\frac{-E_a + qV_{oc}}{nkT}\right)}{1 + \frac{\Delta f}{f_{sc}} - \frac{\chi}{f_{sc}}V_{oc}}. \tag{A6}$$

The ideality factor is then obtained from the logarithmic slope of the $V_{oc}(\log(J_{sc}))$ relation according to

$$\frac{1}{n_{\text{voc}}} = \frac{kT}{q} \frac{d}{dV_{\text{oc}}} \log(J_{\text{sc}}) = \frac{1}{n} + \frac{1}{1 + \frac{\Delta f}{f_{\text{sc}}} - \frac{\chi}{f_{\text{sc}}} V_{\text{oc}}} \frac{kT}{q} \frac{\chi}{f_{\text{sc}}} = \frac{1}{n} + \frac{J_{\text{sc}}}{J_{\text{ph}}(V_{\text{oc}})} \frac{kT}{q} \frac{\chi}{f_{\text{sc}}} \quad , \quad (\text{A7})$$

where $J_{\text{ph}}(V_{\text{oc}})$ is the photocurrent density at V_{oc} . Eq. (A4) implies that the ideality factor n_{voc} obtained from this method overestimates the real diode ideality factor n_{id} . However, this failure is relatively small, on the order of tenths of a percent [Eron and Rothwarf, 1984], because usually it holds that $f_{\text{sc}}/\chi \gg kT/q$.

The derivation of Eq. A5 with respect to the external voltage V leads to

$$G = \frac{dJ}{dV} = \left\{ J_{\text{sc}} \frac{\chi}{f_{\text{sc}}} - \frac{J_{00}}{nkT/q} \exp\left(\frac{-E_a + q(V - JR_s)}{nkT}\right) \right\} (1 - GR_s) \quad . \quad (\text{A8})$$

In the open-circuit situation, we have $J = 0$, $V_j = V = V_{\text{oc}}$, and consequently

$$G_{\text{oc}} = J_{\text{sc}} \left\{ \frac{\chi}{f_{\text{sc}}} - \frac{1}{n_{\text{id}} kT/q} \left(1 + \frac{\Delta f}{f_{\text{sc}}} - \frac{\chi}{f_{\text{sc}}} V_{\text{oc}} \right) \right\} (1 - G_{\text{oc}} R_s) \quad . \quad (\text{A9})$$

Rearranging Eq. A9 via

$$G_{\text{oc}} (1 + R_s J_{\text{sc}} \{ \}) = J_{\text{sc}} \{ \} \quad , \quad (\text{A10})$$

$$G_{\text{oc}} = J_{\text{sc}} \{ \} / (1 + R_s J_{\text{sc}} \{ \}) \quad , \quad (\text{A12})$$

$$R_{\text{oc}} = 1/(J_{\text{sc}} \{ \}) + R_s \quad (\text{A13})$$

leads to

$$R_{\text{oc}} = \frac{nkT/q}{J_{\text{sc}} \left\{ 1 + \frac{\Delta f}{f_{\text{sc}}} - \frac{\chi}{f_{\text{sc}}} [V_{\text{oc}} + nkT/q] \right\}} + R_s \quad . \quad (\text{A14})$$

Because $V_{\text{oc}} \gg nkT/q$ and $J_{\text{ph}}(V_{\text{oc}}) = J_{\text{ph}}^{\text{max}} [f_{\text{sc}} + \Delta f - \chi V_{\text{oc}}]$, we can rewrite Eq. A13 by

$$R_{\text{oc}} \approx \frac{nkT/q}{J_{\text{sc}} \left\{ 1 + \frac{\Delta f}{f_{\text{sc}}} - \frac{\chi}{f_{\text{sc}}} V_{\text{oc}} \right\}} + R_s = \frac{nkT/q}{J_{\text{ph}}(V_{\text{oc}})} + R_s \quad (\text{A14})$$

and the ideality factor determined via the $R_{\text{oc}} (1/J_{\text{sc}})$ relationship is given by

$$n_{\text{Roc}} = \frac{n}{\left\{ 1 + \frac{\Delta f}{f_{\text{sc}}} - \frac{\chi}{f_{\text{sc}}} V_{\text{oc}} \right\}} \quad . \quad (\text{A15})$$

Likewise, we may write $n_{\text{Roc}}/n = J_{\text{sc}}/J_{\text{ph}}(V_{\text{oc}})$. Thus, the $R_{\text{oc}}(1/J_{\text{sc}})$ method considerably overestimates the ideality factor. Typical values of the ratio $n_{\text{Roc}}/n_{V_{\text{oc}}} \approx n_{\text{Roc}}/n$ in Fig. 15 amount to a range of 3–4, implying that only 25%–35% of the short-circuit current density is collected under open-circuit conditions.