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Luminescence characterizations and parameter drifts of CIGS solar cells

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ABSTRACT

Lifetime guarantees of more than 20 years are a target for the long-term stability of solar modules. An important point for the future of CIGS solar cells is to understand the impact of metastable behaviour on long-term stability. Accelerated ageing under open-circuit conditions leads to a drop in open-circuit voltage (V_{oc}). A decrease in the net doping density is responsible for the drop in V_{oc} and consequently the drop in the photoluminescence (PL). In the initial state the electroluminescence (EL) ideality factor exhibits a value close to unity, as expected from theory. After the dark anneal an increase in the EL ideality factor is observed, and an EL measurement at constant voltage shows a decrease in EL: both these behaviours are due to a pile-up of negative charges at the heterointerface. The application of a positive bias or an illumination during the endurance test leads to an optimization of stability. This paper shows that PL and EL can distinguish between bulk and interface properties and are well suited for the detection of degradation mechanisms.

Introduction

The importance of CIGS in terrestrial photovoltaics is steadily increasing [1–3]. A significant aspect of all PV technologies is long-term stability, which can be assessed by accelerated ageing. This paper presents the use of luminescence techniques, in particular electroluminescence (EL) and photoluminescence (PL), in a study of the accelerated ageing of CIGS-based solar cells. The electrical characteristics (*I-V*, *C-V*) and luminescence properties were therefore detected before and after dark anneals at elevated temperatures. Furthermore, the EL properties were characterized by measuring the EL intensity as a function of the applied bias. From these curves of intensity versus voltage, diode parameters – such as an EL ideality factor – were extracted. The parameter drifts obtained were compared to simulation results utilizing SCAPS (a solar cell capacitance simulator developed at the University of Ghent, Belgium).

Reliability testing

Endurance tests under different conditions were undertaken in order to investigate the

behaviour of luminescence in the context of accelerated ageing. The tests were done at elevated temperatures of up to 165°C; in some cases a low positive (max. 0.4V) or negative (max. 0.2V) bias was applied to the cells during the endurance test. The devices were annealed for up to 200h. The following parameter drifts were measured before and after the endurance test:

- Open-circuit voltage (V_{oc})
- Fill factor (*FF*)
- EL
- PL
- *C-V* values

PL was detected using a pco.1300 digital 12-bit CCD camera with an exposure time of 10 seconds. For EL, an InGaAs photo detector was used. *I-V* curves were mapped with an Agilent 4155C Semiconductor Analyzer and measured under a halogen spot. The *C-V* measurements were detected with an HP 4192 Semiconductor Analyzer at a frequency of 100kHz. All measurements were taken at a temperature of 300K. The analyzed high-efficiency CIGS solar cells were produced by Manz CIGS Technology GmbH and typically exhibit a V_{oc} of 700mV, an $FF > 72\%$ and efficiencies exceeding 14%.

V_{oc} parameter drifts

Fig. 1 shows the parameter drift of V_{oc} for an applied bias at 165°C. For the long-term test at elevated temperatures, biases of 0.4, 0.2, 0.1 and –0.1V were applied to the cells for 200h during the accelerated ageing. As a reference, a device was dark annealed under open-circuit conditions, and this device shows a decrease in V_{oc} [4]. *C-V* measurements indicate that a decrease in the net doping density is responsible for this degradation.

Fig. 1 shows that a bias during the endurance test influences the V_{oc} parameter drift: a positive bias leads to a stabilization or enhances V_{oc}; a negative bias leads to a decrease in V_{oc}. An endurance test under 0.2 suns also results in stabilization, which leads to the assumption that this is due to an internal bias across the heterointerface [5].

Simulations of PL

All simulations were carried out using SCAPS. From theory it is known that luminescence intensity depends on the splitting of the quasi Fermi levels [6]. In the previous section a decrease in V_{oc} was obtained after the endurance test because of a decrease in the net doping density. In the next section a decrease in *FF* due to a pile-up of negative charges at the interface will be presented. These two mechanisms – V_{oc} and *FF* – affect the electrical characteristics of the device. As a consequence, the splitting of the

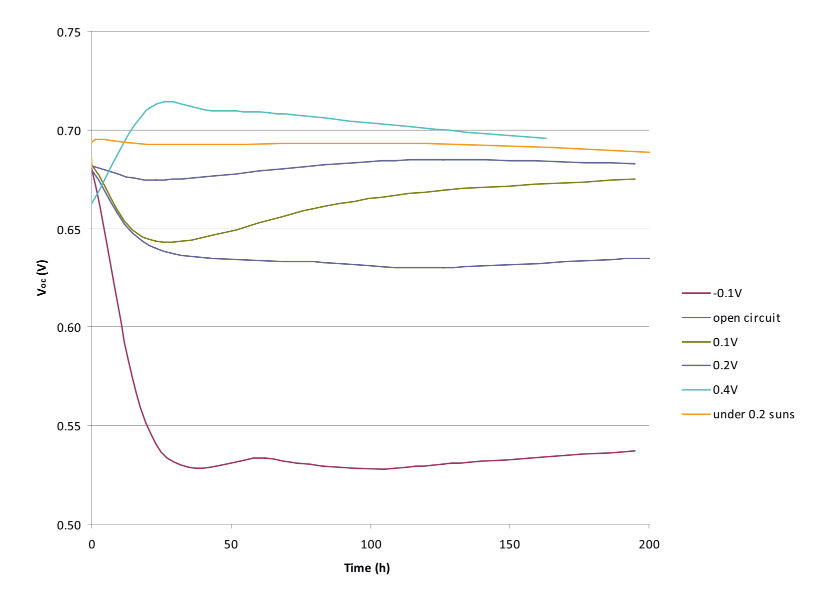

Figure 1. V_{oc} parameter drifts after the endurance tests.

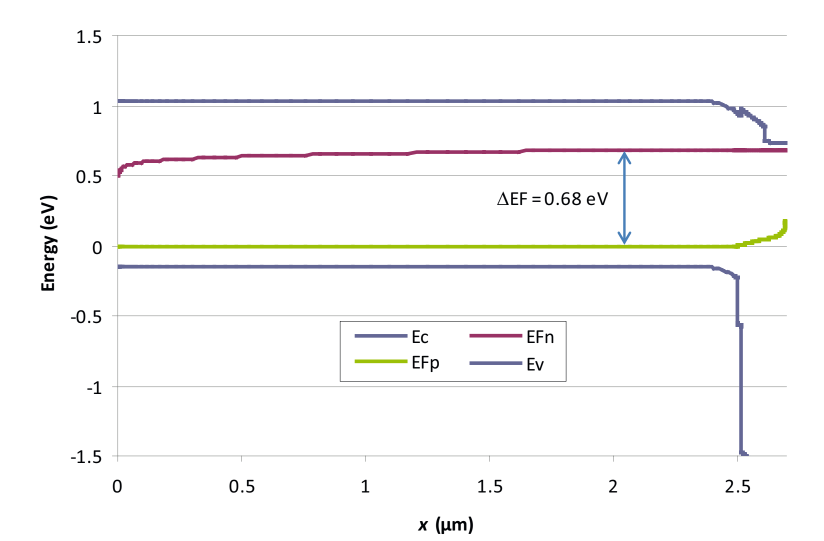

Figure 2. Simulated reference band diagram for PL.

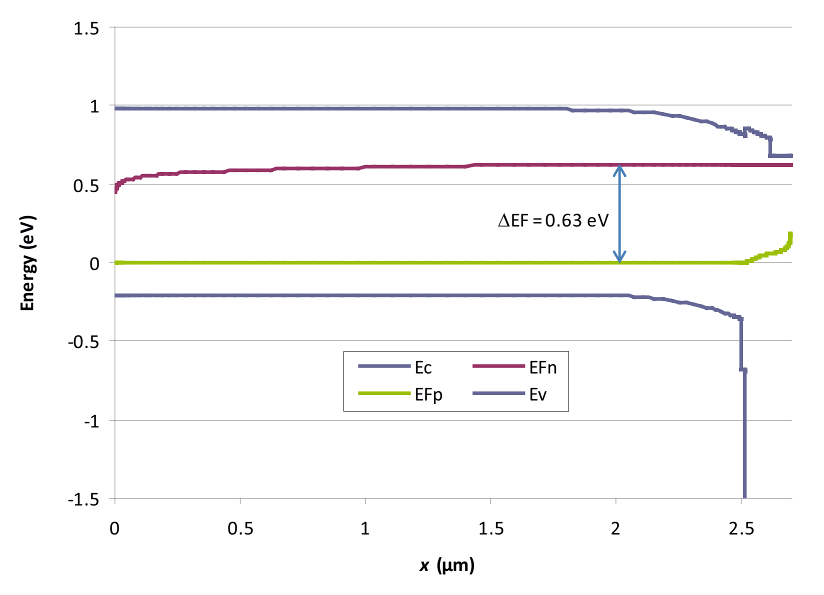

Figure 3. Simulated band diagram for PL with reduced N_A.

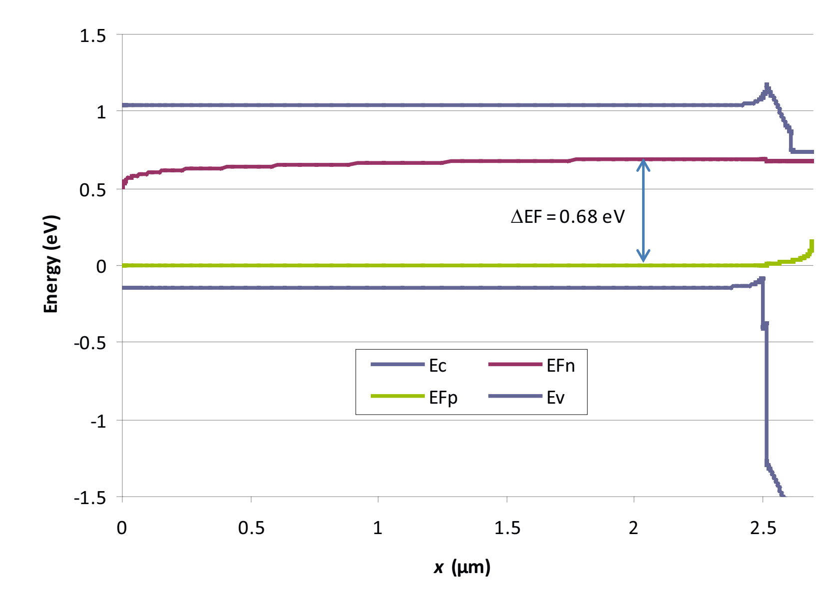

Figure 4. Simulated band diagram for PL with a pile-up of negative interface charges.

Figure 5. Setup for PL measurements.

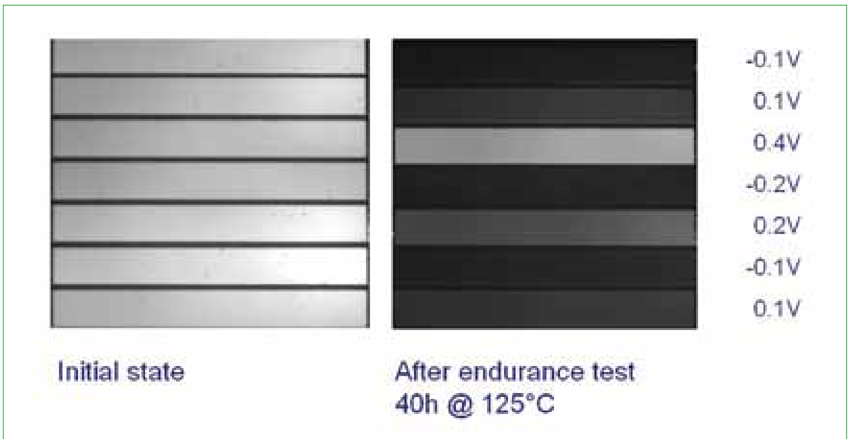

Figure 6. PL images before and after the endurance test.

quasi Fermi levels, and therefore the luminescence intensity, is affected by certain operating conditions.

Fig. 2 shows the band diagram of the heterointerface under illumination and open-circuit conditions which correspond to the measurement configuration of PL. The splitting of the quasi Fermi levels in this reference state at a certain position is roughly 680meV ($\Delta E_F(x=x_0)$ = 680meV). If the net doping density (N_A) is reduced, ΔE_F decreases to 630meV (Fig. 3), resulting in a reduced PL intensity (Φ_{PL}) compared to the reference. A simulation of interface charges (Fig. 4) exhibits no significant change in ΔE_F (680meV) and therefore Φ_{PL} is constant.

Thin Film

Photoluminescence

The theory of PL is well known [7]. In this study the influence of accelerated ageing on PL intensity is investigated. Fig. 5 shows the measurement setup for the PL procedure: a CCD camera was used, and the test device was illuminated by four LED arrays operating at a wavelength of 630nm. In order to separate the luminescence and the excitation wavelength, a GaAs filter with a cut-off wavelength of about 870nm was employed.

> "A positive bias tends to maintain the PL intensity of the initial state, whereas a negative bias or an open-circuit condition reduces the luminescence significantly."

Fig. 6 shows PL images of a device with eight interconnected cells before and after endurance testing for 40h at 125°C. During the endurance test, different low-voltage biases between +0.4V and –0.2V were applied to the cells. In the initial state the PL intensity is homogenous over the whole device. As can be deduced from the figure, the PL intensity is affected by the induced metastabilities. A positive bias tends to maintain the PL intensity of the initial state, whereas a negative bias or an open-circuit condition reduces the luminescence significantly. These results agree with those of the SCAPS simulations, which leads to the conclusion that the underlying ageing mechanism for the PL is the N_A parameter drift, and the PL intensity is therefore governed by the net doping density. *C-V* measurements taken during the investigation confirm this result.

FF parameter drift

The parameter drift of the *FF* was also investigated. Fig. 7 shows the *FF* measured (i) in the initial state, (ii) after a dark anneal at 165°C for 24h, and (iii) after a light soak for 3h following the dark anneal. The devices were measured under illumination through spectral edge filters, which only transmit light exceeding a certain cut-off wavelength. Only illumination with

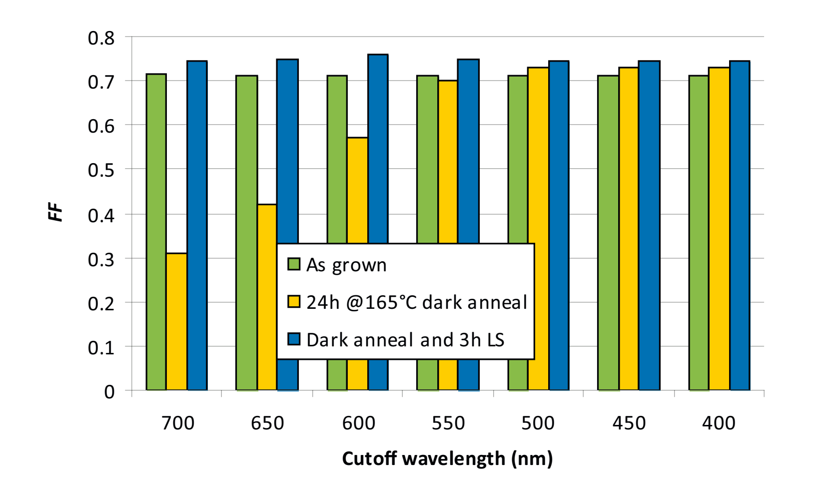

Figure 7. *FF* measured with spectral edge filters after the endurance tests.

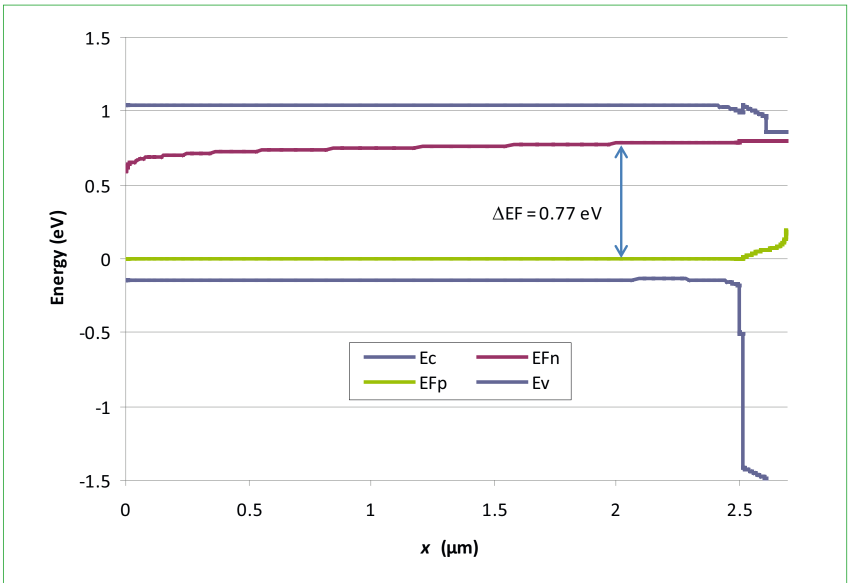

Figure 8. Simulated reference band diagram for EL.

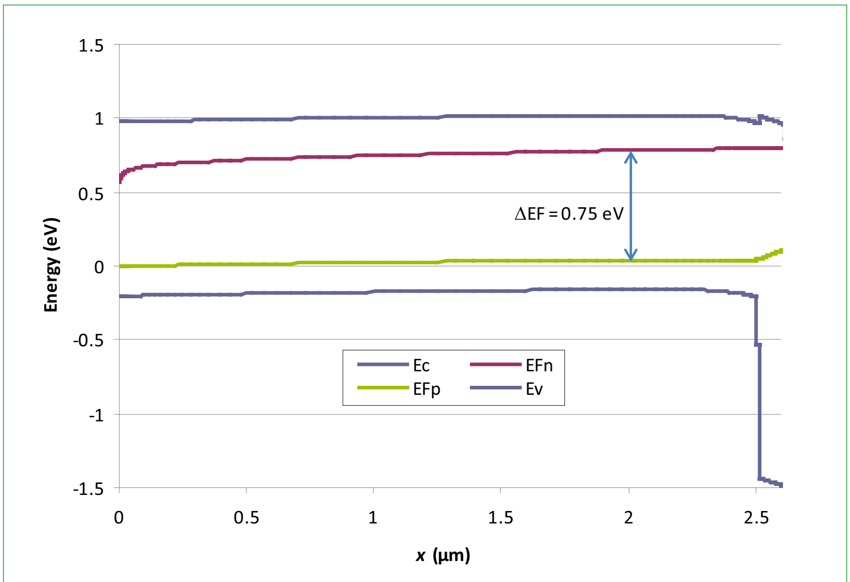

Figure 9. Simulated band diagram for EL with reduced N_A.

wavelengths greater than 550nm shows a decrease in *FF*. This effect is known as the 'blue metastability'. The reason for this behaviour is a pile-up of negative charges at the heterointerface as a consequence of the endurance test, and this restricts the collection of current. An illumination of the CdS buffer (UV) is necessary to avoid this metastable influence, but a light soak can also reverse this effect as shown in Fig. 7.

Simulations of EL

Figs. 8–10 show simulated band diagrams (reference, reduced N_A, negative interface charge pile-up) in the dark, which correspond to the EL situation when a constant bias of 800mV is applied to the device during the measurement. For a reduced N_A, a minor decrease of 750meV in ΔE_F is exhibited, compared to the reference ($\Delta E_F(x=x_0)$ = 770meV), and this results in a relatively unchanged EL intensity (Φ_{EL}). A simulation of interface charges indicates a reduction in ΔE_F (660meV), leading to a decrease in Φ_{EL}.

EL with lock-in amplifier

The fact that the EL is related to the V_{oc} is shown in Kirchartz & Rau [8], but for our study it is desired to correlate the behaviour of EL to the endurance tests. Fig. 11 shows the setup for the EL lock-in measurement: a function generator applies the bias to the sample, and the emitted luminescence is detected by an InGaAs photodiode and amplified by a lock-in amplifier. With this measurement setup it is possible to measure the EL intensity as a function of the applied voltage; the resulting characteristics exhibit similar properties to *I-V* characteristics.

Fig. 12 shows the EL intensity (photodiode current) and applied voltage characteristics. The sample was measured (i) in the initial state, (ii) after a dark anneal at 125°C for 160h, and (iii) after a 4h light soak (including a 2h soak at room temperature, followed by a 2h hot, light soak at 80°C) after the dark anneal. At the end of the endurance test, a reduced EL intensity for the same applied voltage was observed – this decrease in intensity (under constant *V* conditions) indicates transport restrictions at the interface. The results correspond to the SCAPS simulations, leading to the conclusion that the underlying ageing mechanism for EL intensity is due to negative charges at the heterointerface. However, light soaking reverses this degradation mechanism, and the same EL intensity as in the initial state is observed.

As in the case of electrical *I-V* characteristics, an EL ideality factor (derived from the intensity versus the applied bias characteristics) can be defined. In the initial state the EL ideality factor exhibits a value close to unity as expected from theory [9]. After the endurance test an increase in the EL ideality factor is observed, as can be deduced from the slope of the blue curve in Fig. 12, but the light soaking tends to reverse the observed parameter drift of the EL ideality factor. An EL ideality factor greater than one requires

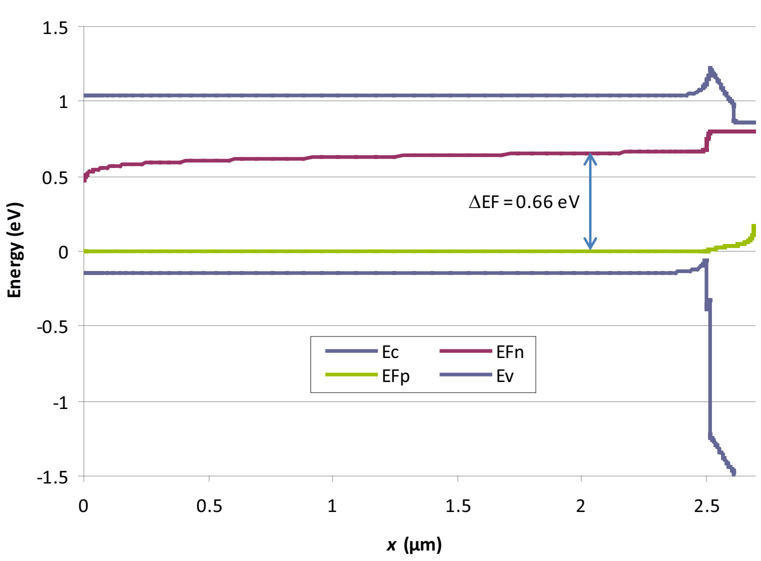

Figure 10. Simulated band diagram for EL with a pile-up of negative interface charges.

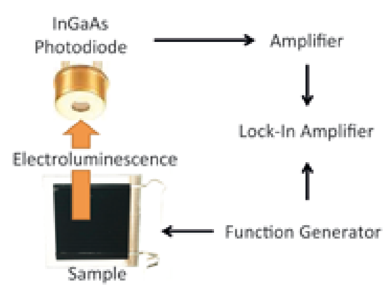

Figure 11. Setup for EL lock-in measurements with an InGaAs photodiode.

that the increase in the externally applied bias does not correspond to the internal increase of the splitting of the quasi Fermi levels, which can be related to interface charges or reduced carrier mobility at the heterointerface. The step in the electron quasi Fermi level (Fig. 10) results from the reduced interface mobility and can be considered as a kind of internal series resistance. As a consequence, depending on the current density, an internal bias drop across this internal series resistance occurs, leading to the rather sharp drop of the quasi Fermi level at the interface. It therefore appears to be possible to separate parameter drifts of bulk properties (N_A) from interface properties (interface charges) by the appropriate operating conditions during the luminescence measurement, i.e. PL or EL under a constant applied bias.

Discussion

The investigations revealed that PL and EL exhibit a metastable behaviour after endurance tests. These findings were correlated with the V_{oc} and *FF* parameter drifts. To obtain the principal degradation mechanisms of the luminescence, the band diagram was simulated for several cases and compared with the measurements. Simulations and measurements of the PL reveal that the net doping density is responsible for this metastable behaviour. For EL (constant voltage) the externally applied bias does not correspond to the internal splitting of the quasi Fermi levels, and therefore interface charges or reduced carrier mobility at the heterointerface is the main degradation mechanism for EL. In the initial state an EL ideality factor close to unity was obtained, but measurements show that this factor is also affected by the metastabilities. Illumination or a bias during the endurance test can enhance or stabilize the cells.

"EL and PL are well suited for the detection of degradation mechanisms and can distinguish between bulk and interface properties."

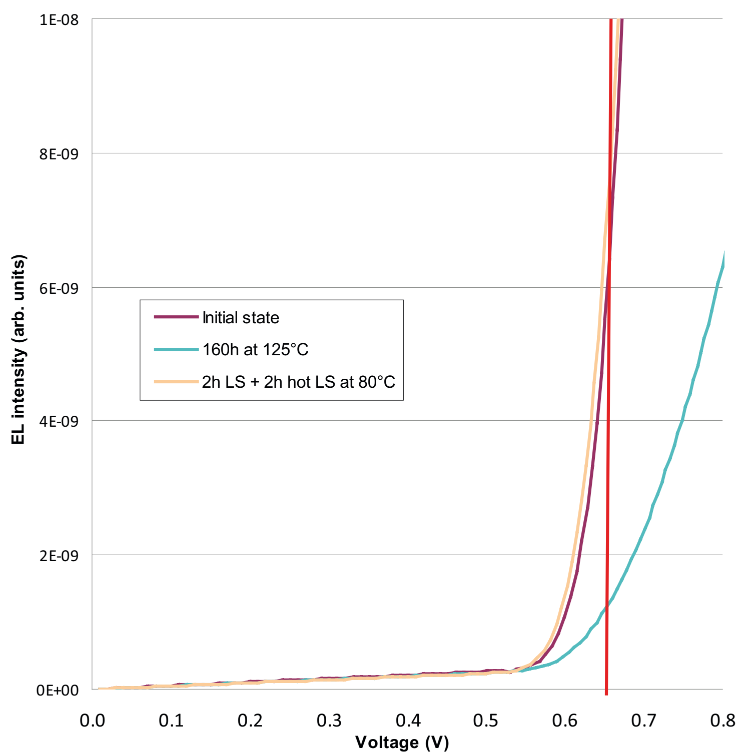

Figure 12. EL intensity versus applied voltage.

Conclusions

Observed parameter drifts of CIGS solar cells after endurance tests included those for EL, PL, *FF* and V_{oc}. The PL intensity was governed by the net doping density, whereas the EL intensity was governed by interface charges. In the initial state the EL ideality factor exhibited a value close to unity, but this factor increased because of negative charges at the interface. The application of a positive bias or an illumination during the accelerated ageing resulted in optimization of the stability. This study has demonstrated that EL and PL are well suited for the detection of degradation mechanisms and can distinguish between bulk and interface properties.

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Thomas Ott received his diploma degree in mechatronics engineering from the University of Applied Sciences Ulm, Germany. Since 2009 he has been working as a research assistant on the RECIS project at the university, where his work focuses on the long-term stability of CIGS thin-film solar cells.

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Raymund Schäffler received his diploma degree in electrical engineering from Stuttgart University, Germany, after which he worked at the university in the field of analytics, TCO and CIGS. This was followed by employment at ZSW Stuttgart (focusing on module technology and encapsulation) and then at Würth Solar. In 2012 he began working for Manz CIGS Technology GmbH as a scientific associate.

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