Observation and implications of the Franz-Keldysh effect in ultrathin GaAs solar cells

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Abstract
Voltage-dependencies were observed in the external quantum efficiency (EQE) spectra of ultrathin GaAs solar cells. The subbandgap tail was shown to increase going from forward to reverse bias, while at energies above the bandgap, voltage-dependent oscillations in the EQE were measured. Using optical simulations, it is irrefutably shown that the voltage-dependencies are caused by the Franz-Keldysh effect, that is, an electric field-dependent absorption coefficient near the bandgap. The dependency on voltage of the subbandgap tail is demonstrated to be strongest in thin-film cells with a textured rear mirror, since the absorptivity below the bandgap is enhanced by light trapping. The voltage-dependent subbandgap tail has important implications for the use of the reciprocity relation between photovoltaic quantum efficiency and electroluminescence. It is shown that the radiative limit for the open-circuit voltage of thin-film cells integrated with light management schemes can be underestimated by more than 25 mV. Consequently, these cells may be assumed to be closer to the radiative limit than they really are.

KEYWORDS
Franz-Keldysh effect, reciprocity, textured solar cells, ultrathin gaas, Urbach tail

1 | INTRODUCTION

In 1958, Franz and Keldysh described in two separate publications the effect of a uniform electric field on the absorbing properties of semiconductors and dielectrics. The electric field distorts the band structure of the material, thereby changing the joint density of states in the valence and conduction band. This leads to oscillations in the absorption coefficient at energies above the bandgap while below the bandgap an exponentially decaying tail is introduced as a result of photon-induced tunneling. When the electron and hole wave functions are confined in a quantum-well structure, the effect is known as the quantum-confined Stark effect. Tharmalingam showed that the absorption coefficient near the bandgap in the presence of an electric field can be described by Airy functions, which capture both the oscillating nature of the above-bandgap absorption coefficient as well as the exponentially decaying subbandgap tail. In Figure 1, we plot the calculated absorption coefficient of GaAs for a range of electric fields using these Airy functions. It shows that both the period and amplitude of the oscillations as well as the extent of the subbandgap tail strongly depend on the magnitude of the electric field.

The Franz-Keldysh effect can therefore be one of the contributors to the subbandgap absorption tail of direct semiconductors, commonly referred to as the “Urbach tail.” Typically, this tail is associated with potential fluctuations due to thermal and structural disorder, of which the latter can be induced by defects and doping. Therefore, high-quality crystalline materials typically exhibit narrow Urbach tails while poly-crystalline, amorphous, and/or highly doped materials possess wider tails. The width of the Urbach tail is commonly described...
Observation and simulation of the Franz-Keldysh effect in ultrathin heterojunction cells

In this work, we report observations of significant voltage-dependencies in the external quantum efficiency (EQE) spectra of several ultra-thin GaAs solar cell structures. First, using on-substrate ultrathin heterojunction cells with different emitter doping levels, we show irrefutably that the voltage-dependencies are caused by the Franz-Keldysh effect. Then, we analyze a thin-film structure with a textured rear mirror and show that in this case, the dependence on voltage of the subbandgap tail is significantly more pronounced due to efficient trapping of sub-bandgap photons. We discuss the implications of this observation for the use of the reciprocity relation between photovoltaic quantum efficiency measured at short circuit and electroluminescence.

### RESULTS

#### 2.1 Observation and simulation of the Franz-Keldysh effect in ultrathin heterojunction cells

The layer structure of the investigated ultrathin heterojunction solar cell is schematically depicted in Figure 2. The structure consists of a 300-nm n-type GaAs emitter interfaced with a p-type InGaP base/back surface field (BSF) and a wide-bandgap n-type AlInP window. The heterojunction architecture allows us to observe band tailing effects originating solely from the n-type emitter, while in an ultrathin homojunction architecture different contribution from the emitter and base may complicate the interpretation of results. Furthermore, due to the low absorber thickness, the depletion region makes up a significant fraction of the absorber layer. Since the Franz-Keldysh effect (electric field-dependence of the absorption coefficient) only affects the absorption of photons in the depletion region, we expect it to be more significant in an ultrathin cell structure. We processed two batches of solar cells according to the structure shown in Figure 2 with emitter doping levels (N_d) of 6x10^{16} cm^{-3} and 1x10^{18} cm^{-3}; henceforth referred to as “lightly doped” and “highly doped,” respectively. The performance metrics of the best cells (with an area of 1 cm^2 and front grid coverage of about 6%) measured under AM1.5G illumination are summarized in Table 1. Although the difference in performance between the two architectures is not the focus of this work, the lower J_{SC} of the highly doped cell can be explained by a slightly lower broadband spectral response, which might be related to a higher interface recombination at the window/emitter interface.

The EQE spectra of the two heterojunction cells are shown in Figure 3, for externally applied bias voltages ranging from a reverse bias of -2.4 V to a forward bias of 0.8 V. Beyond 0.8 V, the voltage-induced dark current starts to become of comparable magnitude to the measured signal which therefore diminishes (see Section 5). Figure 3A shows clear oscillations above the bandgap energy in the EQE of the lightly doped cell, which are largely absent in the highly doped cell. Fur-
Table 1: Photovoltaic parameters of the best ultrathin GaAs/InGaP heterojunction solar cells with different emitter doping levels ($N_d$) measured under AM1.5G illumination

| $N_d$ [cm$^{-3}$] | $J_{SC}$ [mA cm$^{-2}$] | $V_{OC}$ [V] | FF [%] | PCE  |
|------------------|------------------------|-------------|-------|------|
| 6x10$^{16}$      | 18.2                   | 1.040       | 79.2  | 15.0 |
| 1x10$^{18}$      | 17.3                   | 1.050       | 80.2  | 14.5 |

Abbreviations: FF, fill factor; PCE, power conversion efficiency.

Furthermore, in Figure 3A,B, a significant dependency of the subbandgap tail on bias voltage can be observed, again more strongly in the lightly doped cell than in the highly doped cell. In addition, Figure 3B reveals that at long wavelengths, the EQE of the highly doped cell becomes higher than the EQE of the lightly doped cell. The overall lower spectral response of the highly doped cell near the bandgap is due to filling of conduction band states by doping-induced free electrons (the Burstein-Moss effect). By describing the subbandgap tail using a standard Urbach model, the Urbach energy of the lightly doped cell varies from 10 meV at a bias of 0.8 V to around 24 meV at -2.4 V. For the highly doped cell, the Urbach energy is around 17 meV at 0.8 V and also around 24 meV at a bias of -2.4 V.

The results can be explained by the electric field-dependence of the absorption coefficient near the bandgap, as a result of the Franz-Keldysh effect. The dependence on doping might seem counter-intuitive since the peak value of the electric field is higher in the highly doped cell and it is the field that modulates the absorption coefficient and leads to the subbandgap tail and the oscillations in the absorption coefficient. However, the reason that the effect is observed more strongly in the lightly doped cell is that the width of the depletion region is larger and varies more strongly as a function of voltage in this cell. For the lightly doped cell, these depletion region widths in the GaAs emitter for bias voltages of 0.8 V, 0 V, and -2.4 V are 130, 184, and 290 nm, respectively, while for the highly doped cell, they are 20, 27, and 43 nm, respectively. Therefore, the changes of the absorption coefficient induced by the electric field affect a significantly larger fraction of the absorber layer in the lightly doped cell, leading to greater changes in the absorptivity of the absorber as a whole. The fact that the effect is more pronounced in the lightly doped cell also shows that the voltage-dependency of the subbandgap tail is not related to absorption to and voltage-dependent collection from localized subbandgap states. The density of these localized...
states is expected to be higher in the highly doped cell, and therefore the voltage-dependent effects should be more prominent. This is, however, in stark contrast to the observations.

In order to irrefutably show that the observed voltage-dependent effects are due to the Franz-Keldysh effect, we simulated the absorptance of the GaAs absorber layer for a range of bias voltages using the transfer-matrix method. The detailed mathematical approach is outlined in the Supplementary Information; however, the general procedure is as follows. First, the inhomogeneous electric field profile in the GaAs absorber layer was calculated. The changing bias voltage affects both the field strength as well as the width of the depletion region. Therefore, the 300-nm-thick GaAs absorber layer was divided into 60 slices of 5-nm thickness and the local absorption coefficient was computed for each slice based on the calculated electric field profile and the Franz-Keldysh effect. This laminar approach has proven to be accurate for field-dependent simulations of the Franz-Keldysh effect before. The modeled absorption coefficient based on the Franz-Keldysh effect was also convoluted with a subbandgap tail based on a standard Urbach model, to take the structural and thermal disorder-induced band tail into account. Urbach energies of 5 and 15 meV were used for the lightly and highly doped cell, respectively, in line with recent measurements on GaAs thin films. The effect of band filling was taken into account. The thus-obtained absorption coefficient was combined with the real part of the refractive index of GaAs taken from literature, neglecting the influence of the electric field on the latter. The layer structure used in our transfer-matrix code consisted of 92 nm MgF2, 40 nm ZnS, 25 nm AlInP, 60 5-nm-thick layers of GaAs, 100 nm InGaP, and a GaAs substrate. The optical constants of all layers other than GaAs were measured in-house using spectroscopic ellipsometry.

The simulated absorptance curves of GaAs for a range of different bias voltages and two different emitter doping levels are presented in Figure 4. By comparing the simulated absorptance curves directly to the measured EQE spectra, we neglect the effects of carrier collection, thereby solely assessing the effect of bias voltage on the absorption coefficient. Qualitatively, the dependence on bias voltage of the simulated absorptance curves closely matches the EQE measurements shown in Figure 3. For the lightly doped absorber, the above-bandgap oscillations in the simulated absorptance are pronounced, while for the highly doped absorber, they are largely absent (cf. Figures 3A and 4A). A cross-over point in these spectra as a function of voltage is always expected at the bandgap energy due to the nature of the Franz-Keldysh effect. The cross-over point around 840 nm, however, is not trivial and matches very closely to the cross-over point in the measurements. The dependency of the subbandgap tail on bias voltage in the simulated spectra is also stronger in the lightly doped cell compared with the highly doped cell (cf. Figures 3B and 4B). This confirms our statement that the stronger variation of the depletion region in the lightly doped cell is leading to a larger impact of the Franz-Keldysh effect on the absorptance. For long wavelengths, the subbandgap absorptance of the highly doped absorber surpasses that of the lightly doped absorber, as is the case in the EQE measurements.

The oscillations in the EQE spectra as a function of bias voltage imply that at some wavelengths, the absorptance increases with voltage while at other wavelengths the absorptance decreases with voltage. The slope of a monochromatic IV-curve near short-circuit condition can therefore be both positive as well as negative, depending on the illumination wavelength, as was theoretically modeled by Aeberhard. Here, we present measurements of this phenomenon in Figure 5. The most striking behavior is measured in the lightly doped cell (exhibiting a strong Franz-Keldysh effect) at an illumination wavelength of 860 nm (Figure 5A). At this wavelength, the absorptance increases with bias voltage (see Figure 3A). As a result, a positive slope of the IV-curve is measured, until the diode dark current becomes of similar magnitude to the photocurrent. The curves corresponding to subbandgap monochromatic illumination (λ = 890 nm), on the other hand, show a strongly decreasing current as a function of voltage, rendering the IV-curve similar to that of a strongly shunted cell. Here, the absorptance decreases significantly as a function of bias voltage, leading to the observed shape of the curve. The relative effect of the bias voltage on the absorptance is much stronger below the bandgap,

![Figure 5](image-url)
explaining the steeper slope of the curves. Figure 5B shows the same monochromatic measurements on the highly doped cell. It is clear that the voltage-dependence of the absorbance is less pronounced, in line with the EQE measurements shown in Figure 3.

2.2 The Franz-Keldysh effect in cells with a textured rear mirror

The Franz-Keldysh effect was shown to have a significant impact on the EQE spectra of the on-substrate cell architecture shown in Figure 2. Because it is an ultrathin cell structure without a rear mirror, the long-wavelength absorptivity and therefore the maximum efficiency is low, and as a result, the cell structure may not be of much practical significance. However, in general, ultrathin GaAs cells possess advantages over thicker cells in terms of radiation hardness and production cost. When produced in a thin-film architecture, the long-wavelength absorptivity of ultrathin GaAs solar cells can be increased by incorporating a rear mirror, especially when the mirror is textured. In this case, the impact of the Franz-Keldysh effect can be significantly higher due to the strongly increased path length of scattered subbandgap photons, as we will show in the following. We recently described an effective light trapping approach for ultrathin GaAs solar cells based on simple wet chemistry. The cell structure that was employed is schematically depicted in Figure 6. It consists of an ultrathin homojunction GaAs absorber sandwiched between passivating, charge-selective layers and highly doped contact layers. Local Ohmic contact points were fabricated at the rear side to conduct the current while at the same time, the Al0.3Ga0.7As contact layer in between these contact points was manipulated in order to engineer the cell optics. On one half of the wafer, the Al0.3Ga0.7As contact layer was textured using a simple 1-min wet-etching step in-between the contact points. On the other half of the wafer, reference cells with a planar rear mirror were produced by completely removing the Al0.3Ga0.7As contact layer in-between the contact points using a regular polishing etchant. Since the planar and textured cells were processed on the same wafer and therefore originate from the same growth run, the initial material quality was identical.

The performance of these cells is characterized in detail in Van Eerden et al, however, in short, the J_{sc} and PCE of the best planar reference cell were 21.7 mA cm⁻³ and 18.5%, respectively, compared with 24.8 mA cm⁻³ and 21.4% for the best rear-side textured cell. In the present study, we merely show the voltage-dependent EQE spectra of the two architectures in Figure 7. The figure shows that the oscillations above the bandgap energy are again present as shown in the insets in Figure 7B, albeit less prominent than in the EQE spectra that was employed is schematically depicted in Figure 6. It consists of an ultrathin homojunction GaAs absorber sandwiched between passivating, charge-selective layers and highly doped contact layers.

FIGURE 6 Schematic representation of thin-film GaAs solar cells with a planar rear mirror (left-hand side) and a textured rear mirror (right-hand side) that were recently described in Van Eerden et al31 [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 7 Measurements of voltage-dependencies in the external quantum efficiency (EQE) spectra of 300-nm-thick thin-film GaAs solar cells with a planar or a textured rear mirror. (A) EQE spectra on a linear scale for bias voltages ranging from -1.2 to 0.8 V. Inset shows the voltage-dependent subbandgap tail on a logarithmic scale for voltage intervals of 0.4 V. (B) Zoomed-in plots of the EQE oscillations above the bandgap energy for voltage intervals of 0.2 V [Colour figure can be viewed at wileyonlinelibrary.com]
Implications of the occurrence of the EQE

$q$ is the elementary charge, $k$ is the Boltzmann constant, $T$ is the temperature of the cell, $J_{sc}$ is the short-circuit current, $\phi_{sat}(E)$ is the radiative saturation current density of a solar cell in the radiative limit, $\phi_{sat}(E)$ is the solar spectrum, and $\phi_{sat}(E)$ is the blackbody spectrum at the temperature of the cell. $\eta_{ext}$ is the weighted average over all angles of incidence, which is usually similar to the regular EQE for normal incidence.33,34 When the radiative limit for the open-circuit voltage of a solar cell is known, one can assess how closely a given solar cell is operating to this limit by comparing it with a measured $V_{oc}$. Any losses of the measured $V_{oc}$ with respect to the radiative limit can be related to an external luminescent efficiency $\eta_{ext}$ lower than unity according to:\35

$$V_{oc} = V_{db} + \frac{kT}{q} \ln(\eta_{ext}). \quad (2)$$

where $\eta_{ext}$ represents the fraction of all recombination events that leads to emission through the front side of the cell. In recent years, $\eta_{ext}$ has emerged as an important figure of merit for solar cells as it quantifies the optoelectronic quality of a solar cell in one convenient metric. For example, in recent publications by Martin Green,33,36 the radiative properties of record cells from the different PV technologies were characterized by $\eta_{ext}$ while others have stressed the importance of photon recycling for approaching the Shockley-Queisser limit by demonstrating its major impact on $\eta_{ext}$.37,40 and $V_{oc}$.

A general approach to maximize the optoelectronic cell performance while at the same time reducing semiconductor material costs is to utilize cell structures of minimal thickness in combination with different light management approaches to improve the absorption of incident photons.30,41-46 In this situation, physical effects such as the Franz-Keldysh effect that are often overlooked can become relevant and a rigorous quantum mechanical approach is required to properly describe the device physics and identify the performance limits. For ultrathin and nanosstructured GaAs solar cells, this was recently described in detail in previous studies.39,47,48 Most research studies, however, simply apply the photovoltaic reciprocity relation between external quantum efficiency measured at short circuit and electroluminescence under applied bias (Equation (1)) to identify performance limits.33,36-38 The derivation of this reciprocity relation is based on detailed balance between absorption and emission, of which the spectral form is assumed to be independent of bias voltage. This allows the use of EQE spectra measured at short-circuit condition to compute the balance between absorption and emission at open-circuit condition.

As we have shown in this work, however, in ultrathin solar cell architectures, the Franz-Keldysh effect may become significant, making the spectral form of absorption and emission (i.e., the EQE spectra) dependent on bias voltage. In this case, the standard approach of deriving performance limits from the EQE spectra measured at short-circuit condition may lead to significant misinterpretation of the performance limits of a solar cell. This can be rationalized by considering that the Franz-Keldysh effect mainly impacts the near-bandgap and subbandgap part of the EQE. In turn, this part of the EQE affects $J_{sc}$ much stronger than it affects $J_{ph}$, because $\phi_{sat}(E)$ is a steeply increasing function of wavelength in the relevant spectral range. Therefore, the width of the subbandgap EQE tail strongly affects $V_{db}$ and the width of this tail can be dependent on bias voltage due to the Franz-Keldysh effect, as we have shown in this work.

In the following evaluation, we demonstrate the impact of the Franz-Keldysh effect on the determination of $V_{db}$ and $\eta_{ext}$ using measured EQE spectra of the planar and rear-side textured cells shown in Figure 7. In our recent publication31 we used EQE spectra measured at short-circuit condition to calculate $V_{db}$ values of 1.114 and 1.158 V for the textured and planar cell, respectively. Furthermore, based on measured $V_{oc}$ values of 1.027 and 1.015 V, we calculated $\eta_{ext}$ values of 3.5% and 0.4% for the textured and planar cell, respectively, corresponding to a ninefold increase in $\eta_{ext}$ in the textured cell. However, since as a result of the Franz-Keldysh effect, the subbandgap tail is wider at short circuit (high internal field, wide depletion region) than at open circuit (lower internal field, narrow depletion region), we can argue that $V_{db}$ was underestimated and, consequently, $\eta_{ext}$ was overestimated. By measuring EQE spectra as close to open circuit as possible and use these to calculate $V_{db}$ and $\eta_{ext}$, the obtained values should be closer to their true values. We measured the EQE at 0.8 V (closer to open circuit was not possible) and extracted $V_{db}$ values of the textured and planar cell of 1.139 and 1.167 V, respectively, leading to $\eta_{ext}$ values of 1.3% and 0.3%. The obtained values for $V_{db}$ and $\eta_{ext}$ thus significantly differ from the values obtained using the EQE spectra.
measured at short circuit. The difference is particularly pronounced when applying the photovoltaic reciprocity relation to textured cells, since in this case, $V_{dc}$ was underestimated by 25 mV and consequently $\eta_{ext}$ was overestimated by almost a factor of three. This can be understood by considering that small changes in the subbandgap absorption coefficient have relatively large effect on the EQE in textured cells due to the long average path length of scattered subbandgap photons. It can be noted that in reality, the differences will be even larger since we used EQE spectra measured at 0.8 V to calculate $V_{dc}$. At actual open-circuit condition ($V > 1$ V for our cells); however, the subbandgap tail will likely be even narrower. Therefore, the actual $V_{dc}$ and $\eta_{ext}$ will be even higher and thus lower, respectively. Nevertheless, by measuring the EQE as close to open circuit as possible and using these spectra to calculate $V_{dc}$ and $\eta_{ext}$, more accurate values can be obtained than when the standard practise of using short-circuit EQE spectra is employed.

3 | CONCLUSIONS

In this study, the Franz-Keldysh effect was shown to have a significant impact on the external quantum efficiency spectra of ultrathin GaAs solar cells. The electric field in the depletion region modifies the near-bandgap absorption coefficient, leading to oscillations in the EQE above the bandgap energy as well as a varying subbandgap tail as a function of voltage. The effect is more pronounced in cells where a significant fraction of the absorber layer is depleted and the depletion region width varies strongly as a function of voltage, for example, in ultrathin cells with a low absorber doping level. Furthermore, the voltage-dependency of the subbandgap tail is stronger in thin-film cells with a randomly textured rear mirror due to efficient trapping of weakly absorbed photons.

It is demonstrated that the voltage-dependencies have to be taken into account when employing the standard reciprocity relation between photovoltaic quantum efficiency measured at short circuit and electroluminescence. This relation no longer holds when the absorption coefficient is voltage dependent. With device measurements, it is shown that the radiative limit for the $V_{OC}$ of thin-film cells that incorporate light management schemes can be underestimated by more than 25 mV when it is calculated using EQE spectra measured at short circuit. In turn, this leads to an overestimation of the external luminescent efficiency by roughly a factor of 3. Consequently, one may assess these solar cells to be closer to the radiative limit than they truly are. By using EQE measurements made at forward bias to calculate the radiative $V_{OC}$ limit and external luminescent efficiency, these metrics can be determined more accurately. This may yield a better understanding of the true optoelectronic quality of a solar cell.

4 | EXPERIMENTAL

**Solar Cell Fabrication.** The solar cells used in this study were grown using low-pressure metal-organic chemical vapor deposition on 2 inch diameter (100) GaAs wafers, 2° off to (110) orientation. Zn was used as p-type dopant and Si as n-type dopant except for the highly doped n-GaAs contact layer, which was doped using Te. More details on the growth can be found elsewhere. For the on-substrate heterojunction cells, cleaning steps in acetone, water, diluted HCl, water, and isopropanol were followed by standard lithographic techniques to define a resist mask for the front grid. A 250 nm Au front grid and subsequently a 100 nm Au rear contact were then evaporated using electron beam evaporation. The n-GaAs contact layer was then etched in between the front grid using NH$_4$OH:H$_2$O$_2$:H$_2$O (2:1:10 by volume). After another lithography step, etching of the MESA was performed in 25% H$_2$SO$_4$:H$_2$O$_2$ (4:1). The solar cells were finished by evaporating a ZnS/MgF$_2$ antireflection coating using thermal evaporation. More details on the growth and processing of the thin-film cells with a planar and textured rear mirror can be found in Van Eerden et al.

**EQE measurements.** EQE measurements were made using a ReRa SpeQuest system operated with ReRa photon 3.1 software. Light from a Xenon or halogen light source was directed through a monochromator (LOT MSH-300) and chopper and subsequently focussed on the cell with a spot size of about 3 mm. The cell response was measured using a lock-in amplifier. Spectra were measured in 5-nm intervals. In the case of the planar and textured thin-film cells, at a bias of 0.8 V, the dark current started to noticeably diminish the measured photocurrent, which is why the EQE was not measured at higher bias voltages. The EQE spectra measured at 0.8 V were normalized to the spectra measured at lower bias voltages by dividing by a constant factor of about 0.98. The spectra of the on-substrate heterojunction cells were not normalized, as these measurements did not yet diminish at a bias of 0.8 V. The EQE measurements were made on solar cells with a front grid, rather than on dedicated gridless areas. The data were therefore corrected for the grid coverage in the illuminated area.

**JV-characteristics.** The current density-voltage characteristics of the finished solar cells were measured with an ABET Technologies Sun 2000 Class AAA solar simulator which simulates the AM1.5G spectrum with a power density of 1,000 Wm$^{-2}$, a Keithley 2601B source meter, and ReRa Tracer 3.0 measurement software. The solar cells were kept at 25°C during measurement using a heating/cooling water thermostat and Pt100 temperature sensing. The setup is calibrated using an ESI-calibrated reference cell before each measurement series. The monochromatic current-voltage characteristics were made using the same setup, but monochromatic illumination was provided by an optical fiber from the EQE system, focused on the cells with a spot size of about 1 mm. These measurements were performed in a dark environment.

**Transfer-matrix simulations.** Calculations of the bias-dependent absorptance spectra were performed using a freely available Matlab code from Stanford University.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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