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Computational Study Revealing the Influence of Surface Phenomena in p-GaAs Water-Splitting Cells

Lassi Hällström,* Camilla Tossi, and Ilkka Tittonen



ABSTRACT: A computational model of a photoelectrochemical cell describing the influence of competing surface reactions to the operation of the cell is presented. The model combines an optical simulation for the incident light intensity with fully self-consistent solution of drift-diffusion equations to accurately calculate the electronic state of the semiconductor electrode in a photoelectrochemical cell under operation. The solution is calculated for the full thickness of a typical wafer, while simultaneously solving the thin surface charge region with sufficient precision. In addition to comparing the simulated current–voltage response with



experimental data, the simulation is shown to replicate experimental results from electrochemical impedance spectroscopy (EIS) measurements. The results show that considering optical losses in the system is crucial for accurate simulation. The model is capable of selectively characterizing the impact of material parameters on both current–voltage response and interface capacitance, while revealing the internal dynamics of the quasi-Fermi levels that are inaccessible by experimental methods.

■ INTRODUCTION

Photoelectrochemical (PEC) water splitting is a promising pathway to store solar energy in a chemical form, making it possible to produce carbon neutral fuel.¹⁻³ Since its discovery and early developments in the 1970s,^{4,5} it has drawn increasing attention, both in terms of major improvements in efficiency and durability and in terms of the theoretical understanding of the physics behind the phenomenon.⁶ While the basic operational principles of a photoelectrochemical cell are wellknown,¹ understanding the dynamics of the charge transport in the photoactive material and the charge transfer to the electrolyte is still under investigation.^{6,7} While the nominal free energy required to split water is 237.24 kJ/mol, resulting in a minimum electron potential of 1.23 eV, various losses must be taken into account.8 Both hydrogen and oxygen evolution reactions have overpotentials that depend on the quality of the catalyst used to drive the reaction, and some of the photoexcited electron-hole pairs are lost in the recombination processes both in the bulk semiconductor and at the surface.9,10

While the chemical reactions between the light-harvesting materials and the electrolyte are usually modeled using density functional theory (DFT) or Green's function-based methods, $^{11-13}$ these approaches are not feasible to simultaneously simulate the combined effects of all relevant processes in an operational PEC cell. In addition to the overpotentials necessary to drive the chemical reactions and the losses in the semiconductor, some of the incident illumination is lost to reflection or absorption before it reaches the active part of the cell.^{8,14} In a typical laboratory implementation of a photo-

electrochemical water-splitting cell, such as the one used in this work, the incident light has to travel through a glass window and the liquid electrolyte before reaching the electrode.

GaAs is one of the oldest and most studied semiconductor materials applicable to water splitting^{15,16} and to other lightharvesting devices,^{17,18} thanks to its suitable band gap of 1.4 eV and good alignment of the valence and conduction band edges with the water-splitting reaction potentials. They have been shown to achieve high efficiencies in water splitting while retaining relatively simple structure $^{19-21}$ and, on occasion, also high stability.^{22,23} In order to accurately estimate the overpotentials, knowledge of the potential of the valence and conduction band edges with respect to the reaction potentials is crucial.^{24,25} Both experimental and theoretical investigations are extensively available in the literature, 20,26,27 and a significant amount of work exists concerning modeling the carrier dynamics and the current-voltage response in photoelectrochemical cells, in general, utilizing a variety of different approaches.^{6,8,26,28–30} Recently, also simulating electrochemical impedance spectroscopy (EIS) or Mott-Schottky response of the cell has gained some attraction, but these are so far limited to analytic models.^{7,31}

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We present this work that focuses on investigating the band structure of p-doped GaAs at the solid-electrolyte interface, by combining experimental measurements of the photoelectrochemical cell with a numerical model describing the photoinduced carrier generation, mass transfer in the semiconductor, and carrier transfer dynamics at the semiconductor-electrolyte interface. The simulation combines a fully self-consistent solution of the drift-diffusion equations with an optical model that accounts for illumination losses. Our work improves upon previous simulations by simultaneously reproducing both current-voltage (I-V) and Mott-Schottky curves of experimental results for up to moderately degenerate doping densities of the semiconductor electrode. The simulation is then used to explain the experimentally observed difference between the flat band voltage and the photocurrent onset voltage, and the cause of this separation is attributed to the combined effects of surface recombination and reaction kinetics. Furthermore, the results allow us to get insights into the charge carrier dynamics inside the semiconductor and independently characterize the impact of surface recombination and reaction driving photocurrent density kinetics.

MATERIALS AND METHODS

Computational Methods. For symbol definitions see Table 1, material parameters are described in Table 2. The carrier dynamics in the semiconductor are modeled by selfconsistently solving a system of equations derived from the drift-diffusion equations for both carriers, along with Poisson's equation for electrostatic potential

$$\frac{\partial n}{\partial x} = -\frac{1}{qD_n}j_n + \frac{\mu_n}{D_n}n\mathcal{E}$$
(1)

$$\frac{\partial p}{\partial x} = -\frac{1}{qD_{\rm p}}j_{\rm p} - \frac{\mu_{\rm p}}{D_{\rm p}}p\mathcal{E}$$
⁽²⁾

$$\frac{\partial j_n}{\partial x} = -q[G(x) - R(x)] \tag{3}$$

$$\frac{\partial j_{\rm p}}{\partial x} = q[G(x) - R(x)] \tag{4}$$

$$\frac{\partial \mathcal{E}}{\partial x} = \frac{\rho}{\varepsilon} \tag{5}$$

$$\frac{\partial \phi}{\partial x} = \mathcal{E} \tag{6}$$

These equations are self-consistently solved for six variables as functions of the position x: the carrier densities n and p, the electric current densities j_n and j_{p} , the electric field \mathcal{E} , and the electrostatic potential ϕ . Here, eqs 1 and 2 describe the gradients of the carrier concentrations: q is the elementary charge, D is the diffusion coefficient, the carrier fluxes, μ are the carrier mobilities, and \mathcal{E} is the electric field. Equations 3 and 4 are the gradients of the electric current densities in both bands, which depend on the carrier photogeneration rate G(x)and the bulk recombination rate R(x). Equation 5 is the Poisson equation describing the dependence of the electric field on the total charge density ρ , and finally, eq 6 is the relation between the electrostatic potential and the electric field. The equations are solved for the full wafer thickness from x = 0 at the semiconductor-electrolyte interface (SEI) to x =

Table 1. Symbols

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symbol	unit	Description
В		band index denoting either electrons or holes
c _n		electron trap capture coefficient
c _p		hole trap capture coefficient
Ċ	F	Capacitance
D	М	distance from electrolyte interface
3	V/m	electric field
$E_{\rm f}$	eV	Fermi level
EP	eV	hole guasi-Fermi level
E _{ec}	eV	Fermi level in dark equilibrium
E _p	eV	photon energy
Ğ	$s^{-1} m^{-3}$	carrier generation rate
J	A/m^2	electric current density
j ^b	A/m^2	current density in band b
j _n	A/m^2	electron current density
j _p	A/m^2	hole current density
j _d	A/m^2	dark current density
j _{ph}	A/m^2	photocurrent density
j _r	A/m^2	effective current density due to surface recombination
j _p	A/m^2	hole current density
N	m^{-3}	electron density
<i>n</i> ₀	m^{-3}	equilibrium carrier density
n ^b	m^{-3}	carrier density in band b
n _i	m^{-3}	intrinsic carrier density
n _t		number of occupied electron trap states
$N_{\rm A}$	m^{-3}	p-type doping density
N_{T}	m^{-3}	trap state density
Р	m^{-3}	hole density
$p_{ m t}$		number of occupied hole trap states
Р	W/m^2	power density
Q	С	elementary charge
R	$s^{-1} m^{-3}$	recombination rate
R _s	$s^{-1} m^{-2}$	surface recombination rate
S		surface recombination coefficient
S	m/s	surface recombination velocity
V	V	Voltage
$V_{\rm fb}$	V	flat band voltage
$V_{ m ref}$	V	voltage measured versus RHE
$V_{th} = k_B T/q$	V	thermal voltage at 300 K
X	М	distance form electrolyte interface
А		charge-transfer coefficient
$\varepsilon = \varepsilon_0 \varepsilon_r$	F/m	electrical permittivity
Н	V	overpotential
Λ	М	wavelength
$\lambda_{ m gap}$	М	wavelength at material band gap
Р	C/m^{-3}	charge density
$ ho_{ m s}$	C/m^{-3}	surface excess charge density
Φ	V	electrostatic potential
ϕ_0	V	electrostatic potential at the back surface
$\phi_{ m sc}$	V	electrostatic potential drop in the semiconductor
Φ	$s^{-1} m^{-2}$	photon flux density
Х	eV	electron affinity

 $350 \ \mu m$ at the rear contact. At the SEI, the current depends on the total charge carrier flux through the boundary. There are three distinct contributions to the flux: the dark current, the photocurrent, and the surface recombination. Out of these, the dark current and photocurrent contribute to the experimentally measurable electrical current, while the carrier flux due to surface recombination is lost and cannot be exploited. The

Table 2. Material Parameter Values

symbol	Description	value	source
$\varepsilon_{\rm r}$	relative permittivity	12.9 F m ⁻¹	ref 32
$E_{\rm g}$	band gap	1.42 eV	ref 32
A	absorption coefficient	$5 \times 10^4 \text{ cm}^{-1}$	ref 32
$N_{ m D}$	doping density	$1.2 \times 10^{19} \text{ cm}^{-3}$	wafer manufacturer
$N_{\rm C}$	density of states for electrons	$4.7 \times 10^{17} \text{ cm}^{-3}$	ref 32
$N_{ m V}$	density of states for holes	$9.0 \times 10^{18} \text{ cm}^{-3}$	ref 32
$\mu_{ m n}$	electron mobility	5000 cm2 $V^{-1} s^{-1}$	ref 32
$\mu_{\rm p}$	hole mobility	$320 \text{ cm} 2 \text{ V}^{-1} \text{ s}^{-1}$	ref 32
D_n	electron diffusion constant	$200 \text{ cm} 2 \text{ s}^{-1}$	ref 33
$D_{\rm p}$	hole diffusion constant	$10 \text{ cm} 2 \text{ s}^{-1}$	ref 34
$\tau_{\rm n}$	electron lifetime	5 ns	ref 35
$j_{\rm 0ph}$	photocurrent exchange current density	$4.8 \times 10-4 \text{ mA cm}^{-2}$	fitted
j _{od}	dark current exchange current density	$1.7 \times 10-3 \text{ mA cm}^{-2}$	fitted
pН	electrolyte pH	2	measured
Р	illumination power	1000 W m^{-2}	measured
S	surface recombination coefficient	$2.9 \times 10-23 \text{ cm}^4 \text{ s}^{-1}$	fitted

dark current is carried by the majority carriers and depends on the deviation of the Fermi level from the equilibrium level.^{36,37} For a p-type semiconductor, the dark current density is given by

$$j_{\rm d} = j_{\rm od} \left(e^{E_{\rm f}^{\rm p} - E_{\rm eq}/V_{\rm th}} - 1 \right) \tag{7}$$

where j_d is the dark current density, j_{0d} is the dark exchange current density, E_{qf}^{p} is the hole quasi-Fermi level at the SEI, E_{eq} is the equilibrium redox potential in the electrolyte, and $V_{\rm th}$ = $k_{\rm B}T/q$ is the thermal voltage. The quasi-Fermi levels are computed from the solved carrier densities using the Joyce-Dixon approximation,³⁸ which accurately follows the numerical solution to the Fermi-Dirac integral up to moderately degenerate carrier densities. This is especially important for GaAs, since it is typically doped with doping densities comparable to its effective density of states.³⁹ The photocurrent in a photoelectrochemical cell is carried by the minority carriers and depends on the reaction overpotential, defined as the separation of the quasi-Fermi level and the corresponding reaction potential.⁴⁰ The kinetic model used for the photocurrent driven reaction is the Butler-Volmer equation, with the anodic and cathodic currents coupled to the quasi-Fermi levels of the electrons and holes in the semiconductor.³⁷ All surface effects are included in the kinetic model, which contains the free parameters of the simulation: namely, the exchange current densities j_{0ph}^{b} and the charge-transfer coefficients α^{b} , where the carrier index b is either n or p for electrons or holes. This includes the influence of the protective TiO₂ coating used for the experimental work and can be used to phenomenologically include the effects of different cocatalysts. The photocurrent density is given by

$$j_{\rm ph}^{\rm b} = j_{\rm 0ph} \left(e^{\alpha^{\rm b} \eta^{\rm b} / V_{\rm th}} - 1 \right)$$
(8)

where a symmetric reaction is assumed, resulting in the chargetransfer coefficients $\alpha^{\rm b} = 0.5$ for both bands. $\eta^{\rm b}$ are the overpotentials for both bands, calculated as the difference between the quasi-Fermi levels and the respective reaction Article

potentials. Equation 8 is mathematically equivalent to the commonly used transfer rate constant model³⁰ but is more convenient to use in the implementation where the reaction rates are directly tied to the electrochemical potential of the charge carriers. Finally, the surface recombination is driven by excess carrier concentration at the surface, directly competing with the photocurrent

$$j_{\rm r}^{\rm b} = -qs[n(0)p(0) - n_{\rm i}^{\ 2}]$$
⁽⁹⁾

The constant term s is related to the surface recombination velocity S and the density of surface states via Schockley–Read–Hall (SRH) theory. For a p-type device

$$R_{\rm s} = \frac{np - n_{\rm i}^2}{\frac{1}{c_{\rm p}N_{\rm T}}(n + n_{\rm t}) + \frac{1}{c_{\rm n}N_{\rm T}}(p + p_{\rm t})} \approx S(n - n_{\rm 0})$$
(10)

where *c* are the surface capture coefficients, $N_{\rm T}$ is the number of trap states, and $n_{\rm tr}$ $p_{\rm t}$ is the number of occupied trap states. In this work, the denominator is assumed to be constant so that the recombination rate can be modeled by the simple recombination velocity. The total carrier flux at the SEI for each band is the sum of these three partial fluxes. Defining the SEI as x = 0 results in the boundary conditions

$$j_{\rm d}^{\rm b} + j_{\rm ph}^{\rm b} + j_{\rm r}^{\rm b} + j^{\rm b}(0) = 0$$
⁽¹¹⁾

Additionally, an ohmic contact is assumed on the rear boundary, meaning that the carrier concentrations are equal to their intrinsic values. The last boundary condition is given by the electrostatic potential drop across the semiconductor, which is equal to ϕ_{SC} , as shown in Figure 2. The potential drop



Figure 1. Blue: the AM1.5G spectrum. Black: Simulated transmittance of the illumination through 2 mm of fused silica glass, 20 mm of water, and 5 nm of TiO_2 into the active GaAs layer. Quantum efficiency for transmitted photons with energy above the band gap of GaAs is 72.2%. Shaded area: overlap of the GaAs absorption range and the illumination spectrum.

can be calculated when both the flat band potential and the voltage measured in an experiments versus the reference electrode, V_{ref} are known. The Helmholtz potential is not explicitly included in the model, but instead, the band edge positions are defined using an experimental value of the flat band potential.⁴¹ The remaining boundary conditions are therefore

$$qr_{\rm s}(n^{\rm b}(d) - n_0^{\rm b}) - j^{\rm b}(d) = 0$$
⁽¹²⁾

where r_s is the effective surface recombination velocity and n_0^b are the equilibrium carrier densities



Figure 2. Qualitative schematic of the energy levels in the electrolyte and in a p-type semiconductor under illumination.

$$\phi(0) - \phi_0 + \phi_{\rm SC} = 0 \tag{13}$$

where ϕ is the electrostatic potential, ϕ_0 is the potential at the back surface, and ϕ_{SC} is the potential drop across the semiconductor and

$$\phi(d) - \phi_0 = 0 \tag{14}$$

Here, eq 11 defines the currents at both bands at the SEI as functions of the overpotentials $\eta^{\rm b}$. Similarly, eq 12 defines the carrier concentrations at the ohmic rear contact of the semiconductor. Equations 13 and 14 define the electrostatic potential drop $\phi_{\rm SC}$ across the semiconductor. The value of the reference potential ϕ_0 is arbitrary and is set to 0 for convenience. Since the distance of the Fermi level from the valence band edge at the rear surface ζ is constant, the potential drop $\phi_{\rm SC}$ is given directly by the difference of the measured voltage V_{ref} and the flat band voltage. Therefore, when the V_{ref} is equal to the flat band voltage, the electrostatic potential drop is zero and the band edges are flat. These boundary conditions with the exception of the dark current are independent of the type of the semiconductor doping, allowing the direction of the photocurrent to emerge from the simulation instead of it being fixed by the choice of boundary conditions.

The governing eqs 1, 3, 5, and 6 and the boundary conditions in eqs 11-14 define a boundary value problem that is numerically solved using the solver bvp5c available in the MATLAB computing environment.⁴² The solver utilizes an adaptive sampling scheme, allowing it to solve the equations for the full wafer thickness while maintaining sufficient accuracy close to the SEI where the variables change rapidly. An example of the adaptive mesh is shown in Supporting Information Figure S2. The solution is first found for the dark case using an analytic solution based on the depletion region approximation as a starting point. The solution is then extended by gradually increasing the illumination power while using the previous solution as a starting point for the next iteration with progressively stronger illumination power. The same method is then used for stepping the voltage versus RHE (reversible hydrogen electrode) or any other simulation parameter of interest. The convergence criteria for the solver was set to a relative error of $<1 \times 10^{-7}$. Running on a single Intel Xeon W-2133 processor, the mean time to convergence is 0.25 s for a single point.

The power output of any solar-absorbing device such as solar cells or photoelectrochemical cells directly depends on the amount of light that is absorbed by the semiconductor.⁴³

Specifically, the light intensity affects the electron-hole pair generation rate G(x). The photon flux entering the semiconductor is computed by assuming a normally incident light with a known spectrum that is independent of the light intensity. The illumination power level is defined at the initial air-glass interface of the measurement cell, and the transfer matrix method is used to calculate the fraction of light entering the active material as a function of the wavelength. In order for the simulations to be comparable to experimental data, accounting for illumination power lost as reflection or absorption before light enters the semiconductor is crucial: the losses from the window and the electrolyte in a typical cell are 30% of the incident power depending on the exact geometry and materials, as seen in Figure 1. The implementation of the transfer matrix method used in this work simultaneously accounts for coherent effects in the protective thin-film layer and incoherent transport through the optically thick glass and water layers.⁴⁴ The complex refractive index data of GaAs, TiO2, and water were acquired from refractiveindex.info,⁴⁵ using the data sets by Aspnes et al.,⁵ Siefke et al.,⁴⁶ and Hale and Querry.⁴⁷

Once the photon flux at the semiconductor side of the SEI is known, the carrier generation rate is calculated using the Beer–Lambert law

$$G(x) = \alpha \Phi e^{\alpha x} \tag{15}$$

where α is the absorption coefficient and Φ is the photon flux reaching the semiconductor with photon energy above the band gap of the material, given by

$$\Phi_{a} = \int_{0}^{\lambda_{gap}} \frac{P(\lambda)}{E_{p}(\lambda)} d\lambda$$
(16)

Here, *P* is the power of the light entering the semiconductor, E_p is the energy of the photons, and λ is the photon wavelength. The upper limit of the integration λ_{gap} is the wavelength corresponding to the band gap energy of the semiconductor. The bulk recombination is considered through the minority carrier lifetime model, which for a p-type material is given by

$$R(x) = N_{\rm A} \tau_{\rm n}[n(x)p(x) - {n_{\rm i}}^2]$$
(17)

where $N_{\rm A}$ is the doping density and $\tau_{\rm n}$ is the mean electron lifetime. While this is a good approximation for direct band gap materials such as GaAs, indirect band gap materials might require a more sophisticated consideration.⁴⁸

Even though the steady-state model cannot explicitly describe dynamic behavior such as the EIS response, it is still possible to compare the simulation to results from the EIS measurements. Specifically, the surface capacitance and consequently the Mott–Schottky behavior can be computed directly from the definition of differential capacitance

$$C(V_{\rm ref}) = \rho_{\rm s} V_{\rm ref} \tag{18}$$

where *C* is the capacitance, V_{ref} is the measured voltage versus RHE, and ρ_s is the excess charge density at the surface. The excess carrier densities are found by integrating the difference between the simulated carrier density and the bulk equilibrium value over the depletion region at the SEI. The surface charge density as a function of the measured voltage V_{ref} is given by

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Figure 3. (a) Simulated inverse square of the differential capacitance. The slope of the simulated response follows the analytical model of the Mott–Schottky equation with the doping density of 1×10^{19} cm⁻³, as provided by the wafer manufacturer. However, the corner at the flat band potential is smoothed resulting in a constant offset. This is highlighted in Supporting Information Figure S8. The experimental data give a good fit for doping density of 3.0×10^{19} cm⁻³ using eq 20, which is also reproduced by the simulation. The equivalent circuit used to fit the experimental data is shown in the inset. (b) Simulated currents compared to experimental chopped light measurement. Blue chopped line: experimental data. Green diamonds: simulated *I*–*V* response in the dark. Blue triangles: simulated *I*–*V* response with AM1.5G illumination. Red circles: photocurrent component of illuminated *I*–*V* response. Pink crosses: current lost to surface recombination. (c) Charge carrier fluxes as a function of distance into the semiconductor from the SEI at -1 V vs RHE. Red: electrons, blue: holes, and black dashed line: the net electrical current flow. Positive values indicate flow toward the positive *x*-axis direction. (d) Comparing the simulation to experimental data by Garner et al.²³ The simulated total currents (dashed lines) were computed with lower surface recombination rate $(1 \times 10^{-28} \text{ cm}^4 \text{ s}^{-1})$ and exchange current density $(1.18 \times 10^{-7} \text{ Am}^{-3})$ than the rest of the results presented in this work. (e) Same as (d), but fitted to results by ref 23. (f) Same as (c), but fitted to results by ref 23.

$$\rho_{\rm s}(V_{\rm ref}) = \int_0^d [p(d) - p(x)] dx - \int_0^d [n(d) - n(x)] dx$$
⁽¹⁹⁾

where d can have any value larger than the width of the depletion region. In practice, d needs to be large enough to be located beyond the region near the surface where the carrier density differs from its equilibrium value. For the numerical solution, the exact value of the boundary of the depletion region is not necessarily obvious, so for the results shown here, the value of 1000 nm was used as a limit that will always cover the whole surface charge layer. Since the carrier density settles to the equilibrium value in the bulk semiconductor, increasing the integration limit further than strictly necessary has no significant impact on the calculated charge density. The integration is visualized in Supporting Information Figure S4.

Experimental Methods. In order to compare the simulation results with values obtained from a real device, a p-type GaAs electrode was used, fabricated from a doped wafer from AXT, with a reported doping density of 1.2 cm⁻³. A 10 nm protective layer of titanium dioxide was deposited on top of every sample by means of atomic layer deposition (ALD), from precursors TiCl₄ and H₂O, at a temperature of 120 °C, meaning that the TiO₂ is in its amorphous form.⁴⁹ On the back of the sample, an AuGe-Ni ohmic contact was made by electron beam evaporation (Edwards E306A), with a 5 nm Ni

layer and 100 nm of AuGe, using materials sourced by K. J. Lesker. For electrochemical measurements, the samples were then diced to 1×1 cm pieces and placed into the measurement cell, with a circular area of 4 mm diameter exposed to the electrolyte, giving a surface area of 0.126 cm²; the electrolyte of choice was 0.1 M H₂SO₄ by Honeywell, the counter electrode was a Pt wire by Sigma-Aldrich, and the reference electrode was a HydroFlex hydrogen electrode by Gaskatel. The electrochemical measurements were conducted with a Zahner Zennium Pro electrochemical measurement system. The light source was an Asahi Spectrum HAL-320 W solar simulator. The EIS measurements were performed with a frequency range from 1 Hz to 1 MHz with 20 points/decade at frequencies above 66 Hz and 5 points/decade below 66 Hz. All simulations presented in this work were performed with the AM1.5G spectrum for illumination.

RESULTS AND DISCUSSION

The surface capacitance as a function of the measured voltage $V_{\rm ref}$ follows the Mott–Schottky relationship, where the reciprocal of the square of the capacitance has a linear dependence on the voltage. The slope of this linear relation is inversely proportional to the doping density of the semiconductor, given by the Mott–Schottky equation

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Figure 4. Impact of different parameters on the current—voltage response of the device: (a) surface recombination rate, (b) exchange current density, and (c) illumination power. The black line corresponds to 1 sun illumination, while the black dashed line is the same illumination without considering the optical losses in the glass and the electrolyte.

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon_r A^2 q N_a} \left(V - V_{fb} - \frac{k_B T}{q} \right)$$
(20)

where ε_0 is the vacuum permittivity, ε_r is the relative permittivity of the semiconductor, A is the surface area, and $V_{\rm fb}$ is the flat band voltage. The interface capacitance follows the linear relationship predicted by the Mott-Schottky theory in both the simulations and the experimental results for the plain p-type device, as shown in Figure 3a. The simulation shown in Figure 3a,b was run both with the doping density reported by the wafer manufacturer of 1×10^{19} cm³ and at a higher doping density of 3.2×10^{19} cm³ which gave the best fit to the measured EIS data. The difference in the manufacturer reported doping density and that found from the EIS analysis could be caused by the protective TiO₂ coating on the sample surface. While the difference is clear in the Mott-Schottky plots, the simulated I-V curve was unaffected by the change in the doping density. According to the simulated results, while the total surface charge density and consequently the surface capacitance depend on the doping density according to the well-established Mott-Schottky relationship, the doping density has no significant impact on the quasi-Fermi level at the SEI and therefore the current generated by the device. The EIS measurement gives a good estimate of the flat band potential at 0.65 V versus RHE and thus fixes the band edges. Comparing the flat band potential to the photocurrent onset in Figure 3b shows a significant deviation from the ideal behavior where the photocurrent would start to flow at the flat band potential. This difference can be explained by including surface recombination as an alternative carrier sink to the electrical current flowing out of the semiconductor. By considering the surface recombination, photocurrent and dark current simultaneously, the simulation can reproduce the complete current-voltage behavior observed in experimental systems. Figure 3b shows the experimental current-voltage response of a real device compared to the simulated results. The dark current was simulated with an incident light intensity of 0 W/ m^2 , and it follows closely the unilluminated side of the chopped light voltammetry measurement. The total current under illuminated conditions is calculated as the sum of the dark current and photocurrent, and it is also observed to accurately follow the illuminated part of the experimental chopped light voltammetry curve. It is noteworthy that for a large part of the voltage range, the current contributing to surface recombination is significantly higher than the useful photocurrent: this is due to poor kinetics caused by the lack of cocatalyst on the samples. The slow reaction rate compared to the surface recombination rate results in high applied voltage required for the photocurrent onset and only a small separation of 1 V between the light and dark current onsets.

Due to the lack of good catalyst and poor conductivity of the TiO_2 layer, the efficiency of the samples measured in Figure 3b is rather modest. In contrast, Figure 3c shows a simulated response compared to the highly efficient p-GaAs water-splitting cell by Garner et al.²³ Assuming that the bulk material properties remain constant, two of the factors for the surface reactions must be changed in order for the simulation to reproduce their results: the surface recombination rate from 1 $\times 10^{-18}$ to 1×10^{-28} cm⁴ s⁻¹ and the photocurrent exchange current density from 1.3×10^{-3} to 1.18×10^{-7} A m⁻³. Figure 3e shows that the surface recombination is almost completely prevented and the photocurrent therefore starts with a lower voltage bias. However, since no information on the flat band potential is reported in their paper, we assume the same value we measured from our own samples. This is a significant assumption, and a lower flat band potential could help to explain the lower value of the exchange current density. Alternatively, it is possible that the surface modification not only passivates the surface against surface recombination, but at the same time, it also inhibits the exchange current density. While the reaction kinetics and the flat band potential do influence the photocurrent onset potential, they cannot explain the difference between the simulated and experimental saturated photocurrent densities in Figure 3d,e. Instead, this can be explained by the uncertainties in the incident light intensity in both the simulation and the experimental study. The simulation assumes optical losses based on the geometry of our experimental setup; therefore, the results are not expected to exactly match those measured in different PEC cells. Finally, the dark current coefficient is responsible for the simulated current increasing even after the photocurrent density has saturated. The impact of these uncertainties is shown in Supporting Information Figure S9.

Figure 4 shows in detail how the I-V curve changes with different parameters. Reducing the surface recombination rate shifts the photocurrent onset toward the flat band potential, increasing the efficiency of the cell. Similar results are observed by increasing the exchange current density. This is an expected outcome, since the surface recombination and the photocurrent are the two reactions competing for the same charge carriers and is comparable to what has been reported previously.⁵⁰ However, the two coefficients cannot be reduced





Figure 5. Energy-band diagrams near the SEI at three different voltage biases. (a) Flat band voltage at 0.65 V vs RHE, (b) at 0 V vs RHE, and (c) at -1 V vs RHE. The hydrogen evolution reaction potential is marked with a dashed line across the vertical axis.

to one by simply considering their ratio: while the photocurrent onset can be changed in a similar fashion by adjusting either one while keeping the other constant, the experimental results by ref 23 cannot be explained by either a change in the exchange current density or the surface recombination rate alone. The current-voltage curve in Figure 3b shows a photocurrent onset at -0.2 V with an extremely steep slope for the current increase. By fitting either the surface recombination or the exchange current alone, the photocurrent onset can be matched, but simultaneously, the slope with increased voltage bias is drastically reduced. In order to explain both our own experimental results in Figure 3a and those by ref 23, we need to fit both the surface recombination rate and the exchange current density as separate degrees of freedom to the data sets. This is a reasonable conclusion, since any surface modification can be expected to impact both of these parameters.

At high enough applied bias, in a real device, the current is ultimately limited by mass transfer in the electrolyte, which results in a resistive behavior and thus linear current—voltage characteristics. Our model assumes that in the typical operating regime of the cell, the current is limited by the processes in the semiconductor, so the ohmic loss in the electrolyte is not included in our model. Since, unlike the photocurrent, the dark current is not limited by the carrier photogeneration rate, the dark current predicted by the model grows exponentially toward more negative potentials.

While the band gap of GaAs of 1.42 eV is above the voltage required for water splitting, Figure 4b shows that even with extremely high exchange current density, the cell is almost one volt short of providing current at 1.23 V versus RHE, which would allow driving the full water-splitting reaction with an ideal counter electrode. This is largely due to the conduction band edge being fixed at 0.53 V versus SHE (standard hydrogen electrode) but also due to the photovoltage generated by the semiconductor never reaching the full value of the band gap. Figure 5 shows the energy-band diagrams from the simulation in Figure 3a,b at three different voltage biases. While the hole quasi-Fermi level does exceed the hydrogen evolution reaction potential already at the flat band voltage, the overpotential is too low to produce significant photocurrent. The energy bands, quasi-Fermi levels, and carrier densities are constant close to the SEI, so there are no net carrier fluxes in any direction. The effective photovoltage produced by the device is the separation between the hole quasi-Fermi level at the SEI and the Fermi level at the back contact. As visualized in Figure 2, the back contact Fermi level is equal to the electron quasi-Fermi level in the bulk of the device. At a moderate increase in bias from the flat band voltage to 0 V versus RHE, the bands start to bend and the overpotential is increased. The bending of the quasi-Fermi levels simultaneously result in net carrier fluxes close to the SEI, as shown in Figure 3c. It is noteworthy that unlike in the schematic in Figure 2 that has been widely used,⁹ the majority carrier quasi-Fermi level is not flat at the SEI, but instead it bends with the corresponding band edge. While with increasingly negative voltages, a depletion and eventually an inversion layer is formed at the SEI that increases the separation between the quasi-Fermi level and the band edge, this is not enough to flatten the quasi-Fermi level completely. While both the overpotential and therefore the photocurrent increase with the bias voltage, the photovoltage given by the quasi-Fermi level separation decreases and at high enough bias, eventually becomes negative. This can be seen in Figure 2c, where at -1 V versus RHE, the back contact Fermi level reaches a higher potential than the electron quasi-Fermi level at the SEI, meaning that regardless of the illumination, the semiconductor causes a loss in voltage and consumes power instead of producing it. Figure 3c,f shows the carrier fluxes in the semiconductor for the simple PEC cell without surface modifications and the more efficient device by ref 23. In the first case, the hole flux close to the surface is negative, meaning that the photogenerated holes are flowing toward the SEI. As seen in Figure 3b, this hole flux contributes mostly to the surface recombination and slightly to the dark current. In the case of the surface-modified device where the surface recombination is suppressed, even the holes generated right at the SEI flow toward the rear surface, reducing the losses and increasing the useful photocurrent provided by the device. While extensive work has been done to study the influence of the surface recombination rate specifically,⁵¹⁻⁵⁵ separating the surface recombination from the reaction kinetics during operation under illumination remains a challenge. Most surface modifications or cocatalyst that increase the rate of the watersplitting reaction will simultaneously act as recombination centers and thus increase the surface recombination rate.^{56,5} Since the flat band potential is a critical empirical input parameter to the simulation, the model cannot predict the changes in the flat band potential and consequently the Mott-Schottky relationship as a function of illumination power. Simulating this phenomenon would require computing the band edge positions ab initio using DFT or a similar quantum chemical approach. In addition, while the Joyce-Dixon approximation allows extending the drift-diffusion model to moderately degenerate case, at exceedingly high carrier

densities, the semiconductor parameters depend significantly on the quasi-Fermi level.58 This limits the model to only moderate voltage bias and doping density in order to avoid the accumulation of excessive carrier densities at the SEI, while experimental work is often done in conditions where the carrier density at the SEI is highly degenerate.⁸ Comparing the sensitivity of the current-voltage characteristics to different parameters, it is clear that the operation of the device depends significantly more on the surface conditions such as the parameters defining the reaction kinetics than bulk properties such as the doping density or carrier lifetime. For example, running the simulation with an electron mobility of 3500 cm^{-2} $V^{-1} s^{-1}$ or 45,000 cm⁻² $V^{-1} s^{-1}$ results in negligible change in the current-voltage response. This is expected as the efficiency of the cell largely depends on minimizing the overpotential, which is directly related to the quasi-Fermi level at the SEI and the surface parameters. The losses in the bulk of the semiconductor are comparably small, as seen in Supporting Information Figure S1.

CONCLUSIONS

We present a robust way of simulating the charge carrier dynamics in a photoelectrochemical cell that can reproduce both *I*–*V* and Mott–Schottky behavior of a real PEC cell even in the case of a moderately degenerate semiconductor. While the focus of this study is in p-GaAs cells, the implemented simulation scheme can be applied to other materials or more complex band structures, with some examples shown in Supporting Information Figures S5 and S6. We show that when comparing simulations of photoelectrochemical devices to experimental data, it is crucial to account for the optical losses in the physical cell. Thin films on top of the working electrode can act either as an antireflection coating or a reflective coating depending on the refractive index and thickness of the film. Since the typical illumination is unevenly distributed in terms of wavelength, it is important to consider the coherent light transfer through these thin films. Our results highlight that in order to understand the operation of the photoelectrochemical cell and optimize its efficiency, it is crucial to separate the different processes at the SEI and consider their impact individually. While the rate constants for the three different current mechanisms from eq 11 can describe the effects of a wide range of surface modifications such as passivation layers or cocatalysts, they are empirical constants that must be fitted to experimental data. Unlike most material parameters, no easy way to predict these values is currently known, and in general their values are specific to a single implementation of a photoelectrochemical device. This could be alleviated in future by advances in computational quantum chemistry. Regardless, we believe that the results of this study offer important insights into both the impact of the surface kinetics and the dynamics behind them in photoelectrochemical cells.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c00982.

Details of the implementation of the simulation and extra results (PDF)

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Notes

The authors declare no competing financial interest.

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