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Supplementary material.
Supporting Information

A Theoretical Perspective on Transient Photovoltage and Charge Extraction Techniques

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Derivation of Equation (10)

Starting from fundamental electrical considerations, assuming planar device structure, we have the electrical transient current density given by the sum of the conduction and displacement current

\[ j(t) = J_c(x,t) + \varepsilon \varepsilon_0 \frac{\partial E(x,t)}{\partial t} \]  
(S1)

where \( E(x, t) \) is the electric field inside the active layer, and \( J_c(x,t) = J_p(x,t) + J_n(x,t) \) is the conduction current; the carrier continuity equations for electrons and holes,

\[ -\frac{1}{q} \frac{\partial J_n(x,t)}{\partial x} + \frac{\partial n(x,t)}{\partial t} = G - R_B \]  
(S2)

\[ \frac{1}{q} \frac{\partial J_p(x,t)}{\partial x} + \frac{\partial p(x,t)}{\partial t} = G - R_B \]  
(S3)

and the Poisson equation:

\[ \frac{\partial E(x,t)}{\partial x} = \frac{\rho(x,t)}{\varepsilon \varepsilon_0} \]  
(S4)
Since the total transient current \( j(t) \) is independent of \( x \), Eq. (S1) is the same when evaluated at \( x = 0 \) as at \( x = d \); thus

\[
 j(t) = J_p(0, t) + J_n(0, t) + \varepsilon\varepsilon_0 \frac{\partial E(0, t)}{\partial t} 
\]

(S5)

\[
 j(t) = J_p(d, t) + J_n(d, t) + \varepsilon\varepsilon_0 \frac{\partial E(d, t)}{\partial t} 
\]

(S6)

On the other hand, by integrating Equations (S2) and (S3) with respect to \( x \) over the active layer, we obtain

\[
 J_n(d, t) = qd \frac{\partial \bar{n}}{\partial t} - q[\bar{G} - \bar{B}_B]d + J_n(0, t) 
\]

(S7)

\[
 J_p(0, t) = qd \frac{\partial \bar{p}}{\partial t} - q[\bar{G} - \bar{B}_B]d + J_p(d, t) 
\]

(S8)

Here, we use the notation \( \bar{f} \equiv (1/d) \int_0^d f(x) \, dx \) for the spatial average across the active layer of a general function \( f(x) \); for example, \( \bar{n}d \equiv \int_0^d n(x) \, dx \), etc.

Then, after adding Eq. (S5) and (S6) and making use of Eq. (S7) and (S8), we find:

\[
 j(t) = \frac{qd}{2} \frac{\partial [\bar{p} + \bar{n}]}{\partial t} + q[\bar{R}_B - \bar{G}]d + J_n(0, t) + J_p(d, t) + \varepsilon\varepsilon_0 \frac{\partial [E(0, t) + E(d, t)]}{\partial t} 
\]

(S9)

In order to eliminate \( E(0, t) \), we continue by also integrating Eq. (S4) with respect to \( x \) over the active layer:

\[
 E(0, t) = E(d, t) - \frac{\bar{p}d}{\varepsilon\varepsilon_0} 
\]

(S10)

where \( \bar{p}d \equiv \int_0^d \rho(x) \, dx \). Furthermore, after noting that

\[
 \frac{\partial V}{\partial t} = \frac{\partial}{\partial t} \int_0^d E(x, t) \, dx 
\]

(S11)

we can rewrite \( E(d, t) \) in terms of the voltage \( V(t) \) across the active layer by integrating the Eq. (S11) by parts, and making use of Eq. (S4), as

\[
 \int_0^d E(x, t) \, dx = E(d, t)d - \int_0^d x \frac{\rho(x, t)}{\varepsilon\varepsilon_0} \, dx 
\]

(S12)

Finally, using Eqs. (S10)-(S12) to eliminate \( E(0, t) \) and \( E(d, t) \) in Eq. (S9), and equating Eq. (S9) with the spatial average of Eq. (S1), it follows that

\[
 \bar{J}_c = j(t) - \frac{\varepsilon\varepsilon_0}{d} \frac{\partial V}{\partial t} = \frac{qd}{2} \frac{\partial [\bar{p} + \bar{n}]}{\partial t} + q[\bar{R}_B - \bar{G}]d + J_{surf} + \frac{\partial \sigma_{el}'}{\partial t} 
\]

(S13)
where $J_{\text{surf}} \equiv J_n(0, t) + J_p(d, t)$ and

$$\sigma'_{el} \equiv \frac{1}{d} \int_0^d \left[ x - \frac{d}{2} \right] \rho(x, t) \, dx$$  \hspace{1cm} (S14)$$

In the case when parasitic leakage currents are present in the device, the total (measurable) device current will behave as if an additional Ohmic conduction current, characterized by the shunt resistance $R_{sh}$, is flowing in parallel to the diode current; this is accounted for by adding an additional current component $V_D/R_{sh}$ into the right hand side of Eq. (S13).

**The dark capacitance in case of a doped active layer**

Consider a $p$-doped active layer (the case with a n-doped layer is completely analogous). Under these conditions, the device in the dark is dominated by doping-induced free holes and negatively charged ionized $p$-dopants (assumed to be fixed), resulting in the formation of a space charge region (depleted of holes) adjacent to cathode. In this case, the space charge density is given by $\rho(x, t) = q[p(x, t) - N_p]$, where $N_p$ is the concentration of ionized dopants and

$$p(x, t) \approx \begin{cases} N_p, & x < d - w \\ 0, & x \geq d - w \end{cases}$$  \hspace{1cm} (S15)$$

in accordance with the depletion layer approximation, where

$$w = \frac{2\varepsilon \varepsilon_0}{qN_p} [V_{bi} - V]$$  \hspace{1cm} (S16)$$

is thickness of the depletion region and $V_{bi}$ is constant.

In accordance with Equation (21) (in the main text), the capacitance is given by

$$C = \frac{\varepsilon \varepsilon_0}{d} + qd \frac{\partial}{\partial V}[n_{\text{eff}}]$$  \hspace{1cm} (S17)$$

where $n_{\text{eff}}$ is given by Equation (15) (in the main text):

$$n_{\text{eff}} = \frac{1}{2} [\bar{p} + \bar{n}] + \frac{1}{q\varepsilon_0} \int_0^d \left[ x - \frac{d}{2} \right] \rho(x, t) \, dx$$  \hspace{1cm} (S18)$$

In case of a $p$-doped active layer, however, we have $\bar{p} \gg \bar{n}$, whereas $N_p$ is assumed to be independent of the voltage; therefore,
\[ q d \frac{\partial n_{eff}}{\partial V} = q \frac{\partial}{\partial V} \left[ \frac{1}{d} \int_0^d x p(x, t) \, dx \right] \approx -q N_p \left[ 1 - \frac{w}{d} \right] \frac{\partial w}{\partial V} \quad (S19) \]

where Eq. (S15) was used in the last step. But from Eq. (S16), we find: \( \frac{\partial w}{\partial V} = -\frac{\varepsilon \varepsilon_0}{q N_p w} \). Equation (S17) is then simplified as

\[ C = \frac{\varepsilon \varepsilon_0}{d} + \frac{\varepsilon \varepsilon_0}{w} \left[ 1 - \frac{w}{d} \right] = \frac{\varepsilon \varepsilon_0}{w} \quad (S20) \]

which is the sought after depletion layer capacitance.

The device model used for the simulations

In the simulations, a numerical 1D drift-diffusion model is used. The model numerically solves Equations (S1) to (S4), where the local conduction current density is taken to follow the laws of drift and diffusion:

\[ J_c(x, t) = J_p(x, t) + J_n(x, t) \quad (S21) \]

\[ J_n(x, t) = q \mu_n n E + q D_n \frac{\partial n}{\partial x} \quad (S22) \]

\[ J_p(x, t) = q \mu_p p E - q D_p \frac{\partial p}{\partial x} \quad (S23) \]

where the electron (hole) mobility \( \mu_{n(p)} \) is assumed to be related to the electron (hole) diffusion coefficient \( D_{n(p)} \) via the classical Einstein relation, \( \mu_{n(p)} = q D_{n(p)}/kT \). The recombination in the bulk is assumed to be second-order, with the net bulk recombination rate being given by \( R_B = \beta [n p - n_i^2] \), where \( n_i^2 = N_c N_v \exp(-E_g/kT) \). \( E_g \) is the effective electrical (donor HOMO - acceptor LUMO) bandgap, whereas \( N_c \) and \( N_v \) are the effective density of transport states for electrons in the acceptor and holes in the donor, respectively. The contacts are assumed perfectly selective and Ohmic for the injection and extraction of majority carriers (holes at the anode, electrons at the cathode); so that, \( J_p(d) = J_n(0) = 0 \), \( p(0) = N_v \) and \( n(d) = N_c \).

The default parameters used in the drift-diffusion simulations are listed in Table S1. Unless otherwise stated these parameters will be assumed.
Table S1. List of default device parameters for the simulations.

| Parameter                                                                 | Value                                      |
|---------------------------------------------------------------------------|--------------------------------------------|
| Photo-generation rate $G_0$ at 1 sun                                      | $6.24 \times 10^{21} \text{cm}^3\text{s}^{-1}$ |
| Second-order recombination coefficient, $\beta$ (10 x reduced relative to Langevin rate) | $1.2 \times 10^{-11} \text{cm}^3\text{s}^{-1}$ |
| Electron and hole mobility, $\mu_n = \mu_p$                              | $10^4 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ |
| Active layer thickness, $d$                                               | 100 nm                                     |
| Relative permittivity, $\varepsilon$                                      | 3                                          |
| Effective density of transport states, $N_c = N_v$                       | $10^{20} \text{cm}^{-3}$                  |
| Electrical bandgap, $E_g$                                                | 1.2 eV                                     |
| Trap density                                                             | -                                          |
| External series resistance, $R_s$                                        | 0 $\Omega\text{m}^2$                      |
| External shunt resistance, $R_{sh}$                                      | $\infty \Omega\text{m}^2$                |
| Hole doping density, $N_p$                                                | 0 $\text{cm}^{-3}$                        |

The voltage dependence of the device capacitance $C$ in the dc (low-frequency) limit for an undoped device in the dark is simulated in Figure S1. Here, the dc limit refers to the limit where the simulated $C-V$ curves no longer changes with decreasing frequency. The capacitance has been normalized to the geometric capacitance of the active layer $C_0 = \varepsilon \varepsilon_0 / d$. Note that trapping and energetic disorder effects have been neglected in the simulations.
In Figure S2, the steady-state electron (blue) and holes (red) densities at open-circuit conditions for different steady-state light intensities are simulated.
The energy level diagrams and quasi-Fermi levels for the different steady-state conditions under illumination, considered in Figure S2, are shown in Figure S3 below. The corresponding energy level diagrams for the thermal equilibrium case is shown in Figure S4.

The energy levels in Figure S3 and Figure S4 are shown relative to the Fermi level of the cathode electrode (at $x = d$).

Figure S2.
Figure S3.

Figure S4.
In Figure S5, the steady-state electron (blue) and holes (red) densities at open-circuit conditions are simulated for the case with a \( p \)-doped active layer under 1 sun steady-state light intensity and under thermal equilibrium conditions in the dark. A concentration of \( N_p = 10^{17} \) cm\(^{-3}\) of ionized dopants is assumed.