

## Supplementary information

### Revisiting lifetimes from transient electrical characterization of thin film solar cells; a capacitive concern evaluated for silicon, organic and perovskite devices.

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#### Device manufacturing

All device fabrication was performed in a N<sub>2</sub> filled glovebox.

The two organic solar cells were manufactured as follows; Photolithographically patterned indium tin oxide (ITO) coated glass substrates were cleaned with water (detergent), acetone and IPA and subsequently oxygen plasma treated for 30 seconds prior to being coated by 30 nm PEDOT:PSS (Clevios™ P VP AI 4083) and annealed for 10 min at 130° C. The P3HT: PC<sub>60</sub>BM active layer was deposited by spin coating at 1500 rpm from a chlorobenzene solution (36 mg mL<sup>-1</sup> total concentration in a stoichiometric ratio of 1:0.8) rendering a film thickness of 150nm. The PCDTBT: PC<sub>60</sub>BM active layer was deposited by spin coating at 800 rpm from a chlorobenzene solution (20 mg mL<sup>-1</sup> total concentration in a stoichiometric ratio of 1:4) rendering a film thickness of 80nm. The devices were completed by thermal sublimation of a low work function electron selective electrode comprising a Ca(3 nm)/Al(110 nm) combination. The OPV solar cells manufactured had an active area of 3 mm<sup>2</sup> as determined by the areal overlap of the employed electrodes.

The MAPI planar perovskite solar cells were fabricated on similar ITO covered glass substrates. Poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)-benzidine (poly-TPD) was spin coated from 1,2-Dichlorbenzene (DCB) solution (7mg/mL) to form the hole selective layer. The perovskite films were then deposited via the well-known two-step inter-diffusion process. In the first step, we used a 600 mg/mL PbI<sub>2</sub> solution (dissolved in N,N-dimethylformamide) with a small amount of CH<sub>3</sub>NH<sub>3</sub>I (molar ratio of 0.2 in reference to PbI<sub>2</sub>). After spin-coating the lead-salt solution, the substrate was annealed for 15 minutes at 70° C. Afterwards, CH<sub>3</sub>NH<sub>3</sub>I (40 mg/mL in 2-propanol) was spin-coated on top and heated at 100° C for 60 minutes. After forming the perovskite layer, PC<sub>60</sub>BM was spin coated from 1,2-Dichlorbenzene (DCB) solution with a concentration of 20 mg/ml followed by 60 minutes annealing at 100° C. In the last step, the substrates were transferred into an evaporation chamber for the final deposition of the electron selective layer comprising 20 nm C60, 8 nm Bathocuproin (BCP) and a 60 nm Au layer. The MAPI solar cells manufactured had an active area of 1.5 mm<sup>2</sup> as determined by the areal overlap of the employed electrodes.

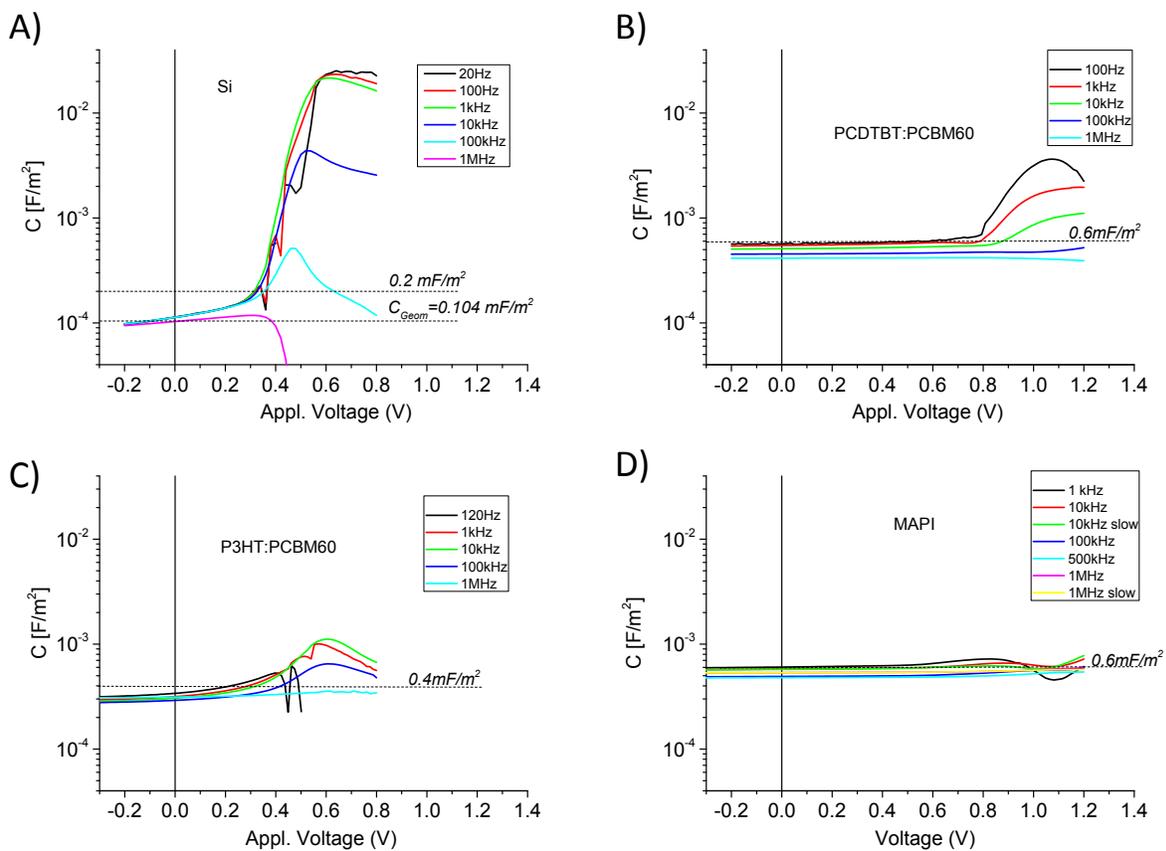
The specifications for the KG-5 filtered Si Photodiode S1787-04 can be found at:  
<http://www.hamamatsu.com/eu/en/product/alpha/P/4103/S1787-04/index.html>

## Characterization methods

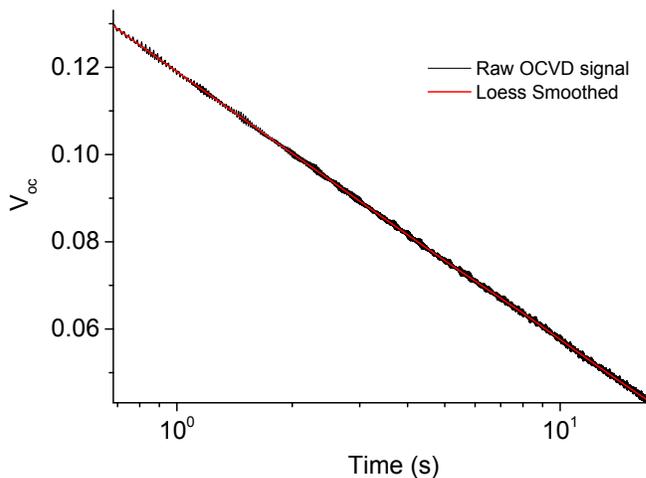
All measurements were conducted inside a closed cycle helium contact gas cryostat apart from the illuminated I-V curves which was executed in a N<sub>2</sub> filled glovebox. The sample was then moved to the cryostat sample holder without ever being exposed to ambient atmosphere. A high power spectrally stable cold LED (Seoul) in combination with 6 Thorlabs ND filters was used to generate the large set of different light intensities spaced in even logarithmic steps for sampling the full  $J_{SC}V_{OC}$  relation. 1 sun equivalent was defined by the LED current matching the same short circuit current density  $J_{SC}$  of a solar cell as measured previously with the sun simulator in the glovebox. The OCVD measurements were conducted by illuminating the cells with the LED for 2 seconds, to rapidly switch it off; employing a home built electrical switch and an Agilent 81150A function generator. The large signal voltage decay of the solar cells over a 1 T $\Omega$  input impedance amplifier (Femto Messtechnik GmbH) was monitored by an Agilent Infinium 90254A digital storage oscilloscope. This high load of the measurement instrumentation is crucial, as it will otherwise have the same effect as having the leaky shunt resistor in parallel. Accordingly, if one intends to correctly monitor the voltage decay of the cell, the measurement load needs to be as high as possible. The OCVD method has so far been sparsely used in the OPV, PbS and perovskite community often to the benefit of the small perturbation method TPV, as it is more straightforward to fit a mono-exponential function to a small signal noisy data than to take the derivative of an equally noisy large signal transient. By employing adjusted sampling frequencies and subsequently selecting suited smoothing functions (Figure S2) for the large signal OCVD data we were however here able to prove that these methods in fact provide quite identical results of determined pseudo first order lifetimes.

The transient photovoltage (TPV) measurements were realized in the cryostat with the high power white light LED and the Thorlabs filters for generating the large set of background bias light illumination. The solar cells were kept under open circuit conditions using the T $\Omega$  impedance. A pulsed Nd:YAG laser ( $\lambda=532\text{nm}$  excitation pulse, 80ps) provided the small optical perturbation generating additional charge carriers in the device. The voltage transients were again recorded by the same digital storage oscilloscope with adjusted sampling settings for each background intensity and the mono-exponential lifetimes were determined as outlined in figure S3.

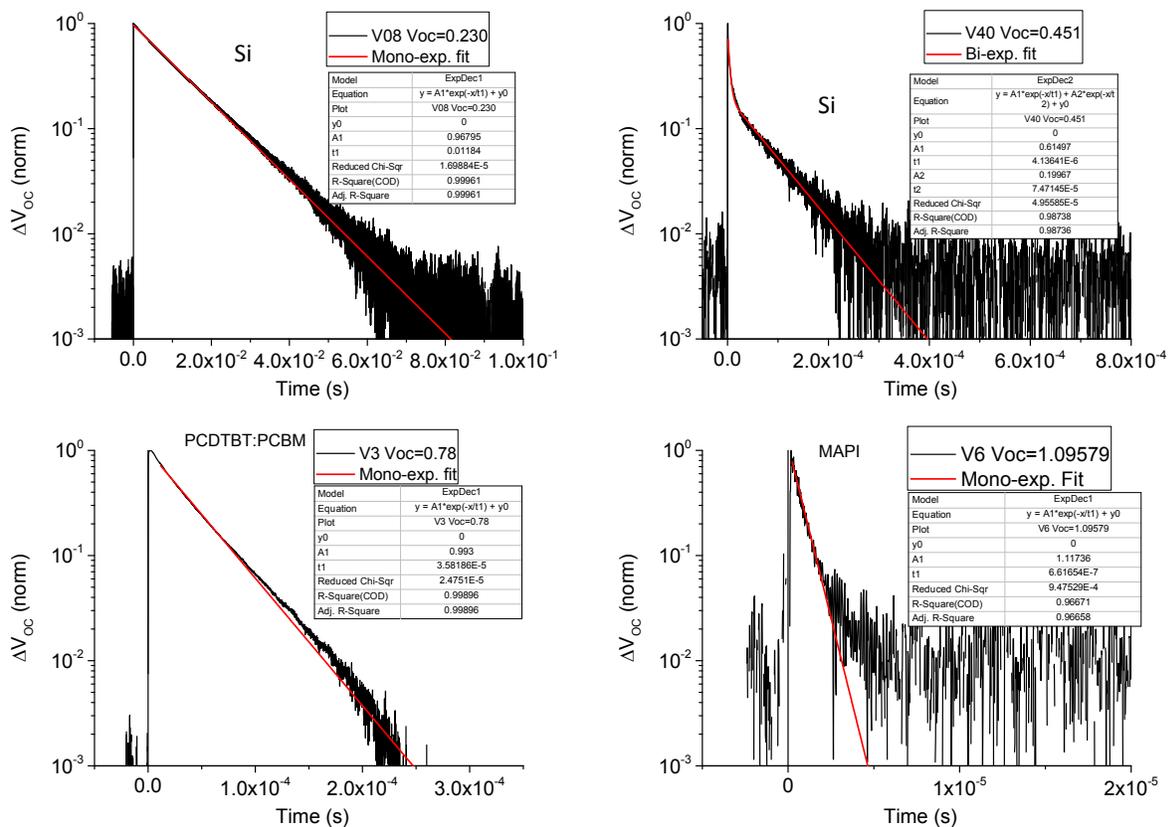
Charge carrier extraction (CE) measurements were performed immediately after each single TPV measurements at the same light intensity. The premeasured  $V_{OC}$  is applied to the solar cell using the function generator (Agilent 81150A) under constant illumination. Triggered by the function generator, the LED was switched off by shortening the constant current source (Keithley 2602) with a high-power transistor. The resulting current transient was pre-amplified by a current amplifier (Femto Messtechnik GmbH) and monitored via the digital storage oscilloscope. Capacitance-Voltage measurements were executed with an Agilent E4980A Precision LCR meter (CV) at various frequencies and modelled in the R<sub>p</sub>C<sub>p</sub> (parallel) mode and outlined in figure S1. The below figures and their corresponding captions summarizes the results referred to in the main manuscript.



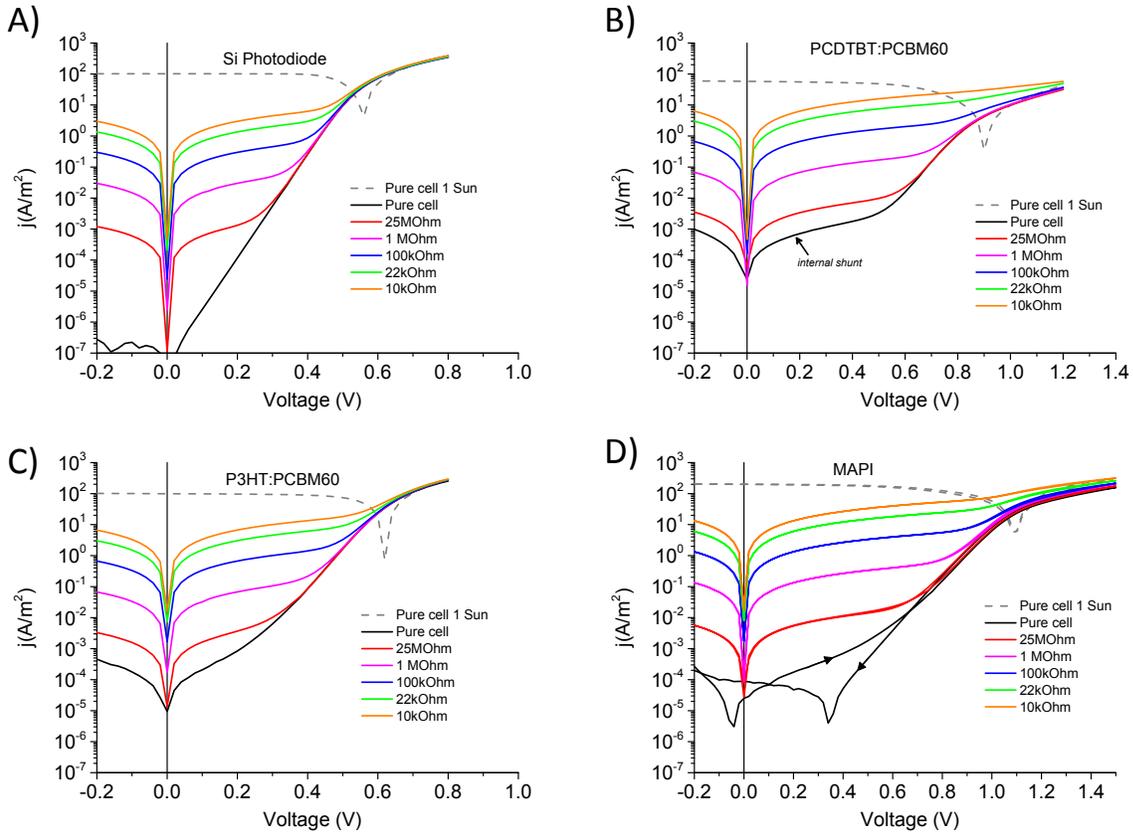
**Figure S1.** Capacitance voltage (C-V) measurements for the four devices evaluated at various frequencies in the parallel mode. The graphs include the single capacitance values used e.g. in the minimum lifetime determination of figure 8 in the main manuscript.



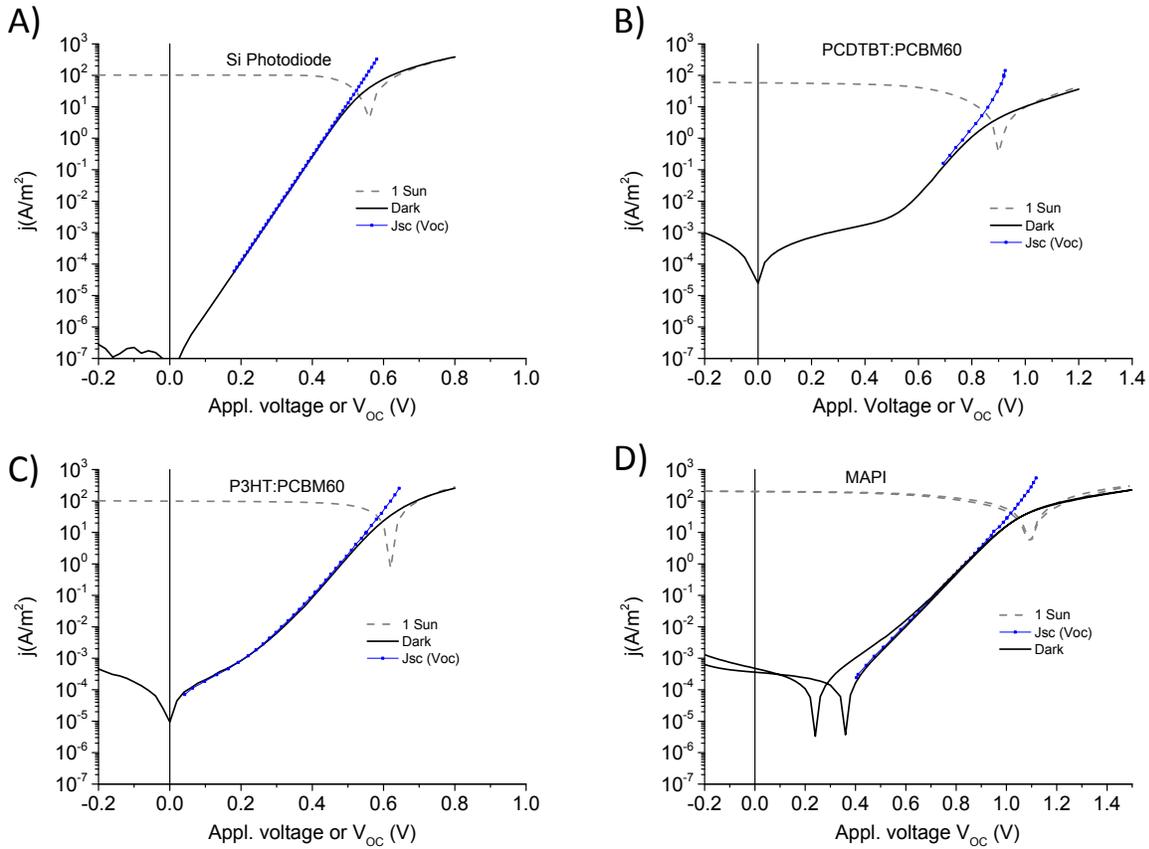
**Figure S2.** Loess smoothing in Origin were conducted for all OCVD measurements. Each performed smoothing was inspected graphically to be well justified (Example shown in figure).



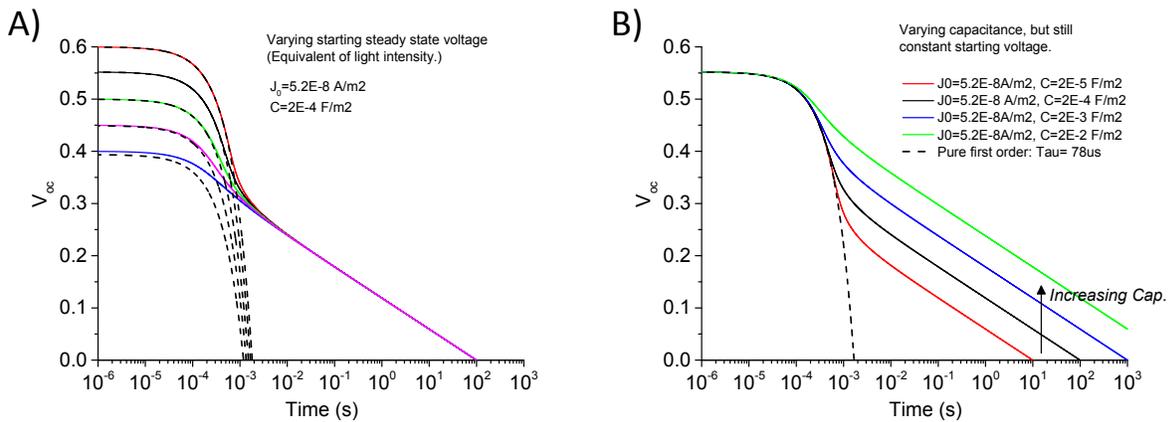
**Figure S3.** Small perturbation transient photovoltage (TPV) examples for some of the devices. The lifetime is determined as earlier by fitting the transients with a mono-exponential decay function. At the highest intensity for the Si cell, bi-exponential functions is instead needed; in those cases the black dots in figure 4 represent the slowest component, equivalent of fitting only the last ~90% of the decay with one mono-exponential.



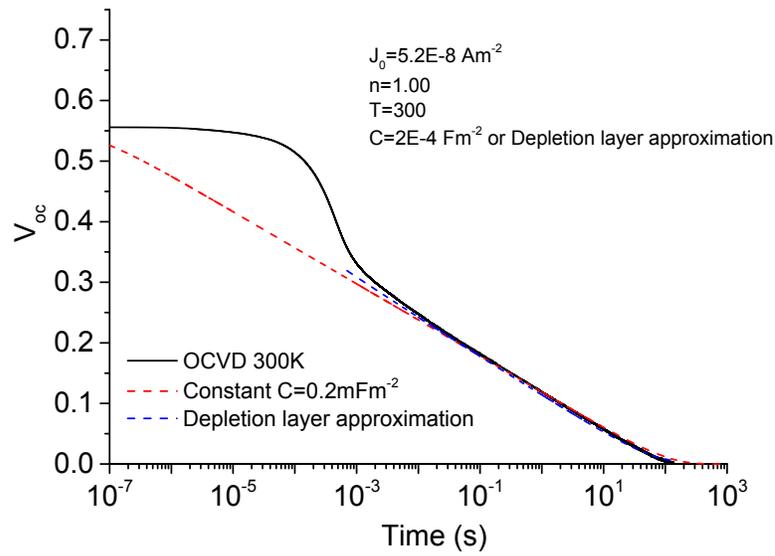
**Figure S4.** Dark IV curves of the four devices when exposed to the shunt resistors as presented in figure 4 of the main manuscript. All but the Si photodiode shows internal shunts that will always speed up the OCVD/TPV decay at lower voltages. The un-shunted MAPI device shows the characteristic “ $V_{OC}$  in the dark” in the reverse sweep, originating from the capacitive charges not disappearing from the device even within the time frame of the double direction I-V sweep.



**Figure S5.**  $J_{sc}(V_{oc})$  data collected at a large set of light intensities allowing to determine the analytical capacitive decay lifetime of figure 8 in the main manuscript. The data is plotted together with dark and illuminated normal IV curves.



**Figure S6.** Analytical low injection regime OCVD traces for a cell with parameters corresponding to the measured mono-crystalline silicon photodiode, under different bias light and capacitances. A constant capacitance was here modelled instead of the slightly voltage dependent depletion layer capacitance. The influence of a constant vs. depletion layer capacitance is presented in the following figure S7.



**Figure S7.** The influence of a constant vs. depletion layer capacitance in the OCVD fitting. The red dashed line embodies a geometric capacitance being fitted (with a factor  $\sim 2$  higher than the true geometric capacitance) to the measured OCVD decay. The blue dashed line is the numerically calculated depletion layer capacitance decay and does not include any fit parameters.