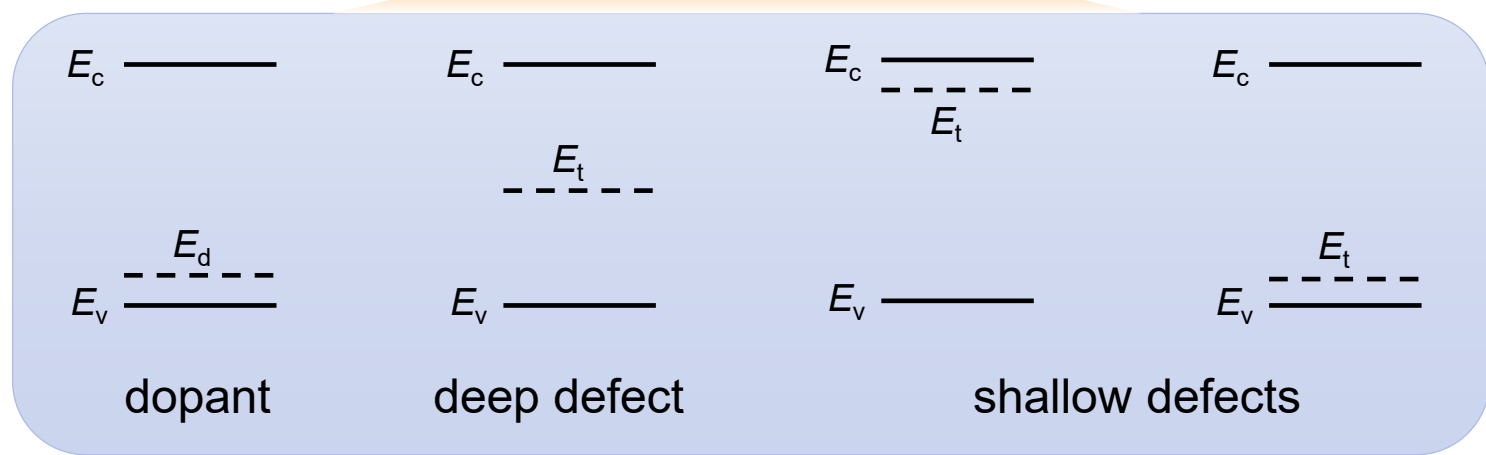
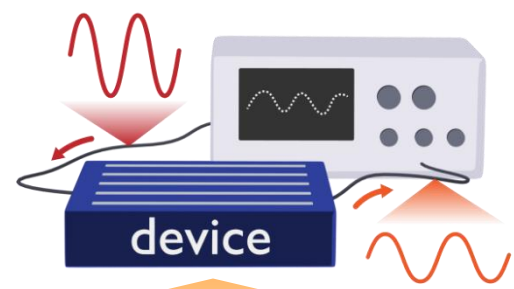


DETERMINING DEFECT DENSITIES AND CHARGE EXTRACTION LOSSES IN PEROVSKITE SOLAR CELLS

Sandheep Ravishankar, Uwe Rau and Thomas Kirchartz

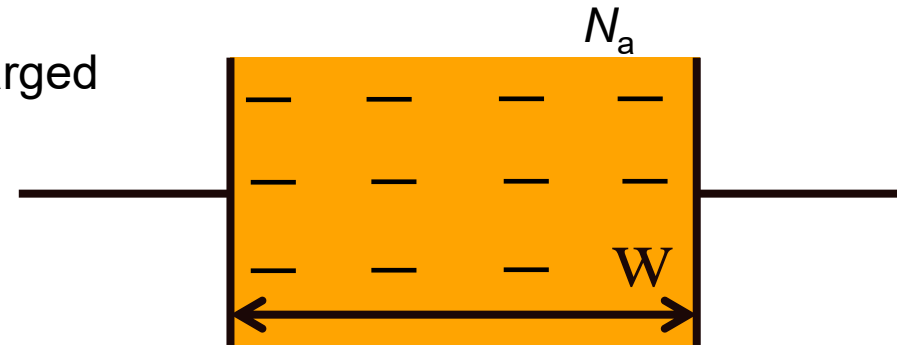
IMD-3 Photovoltaik, Forschungszentrum Jülich

determining doping and defect densities using capacitance measurements

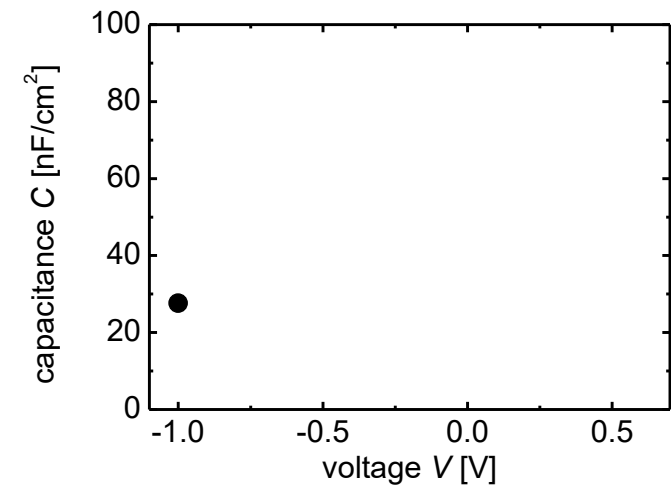
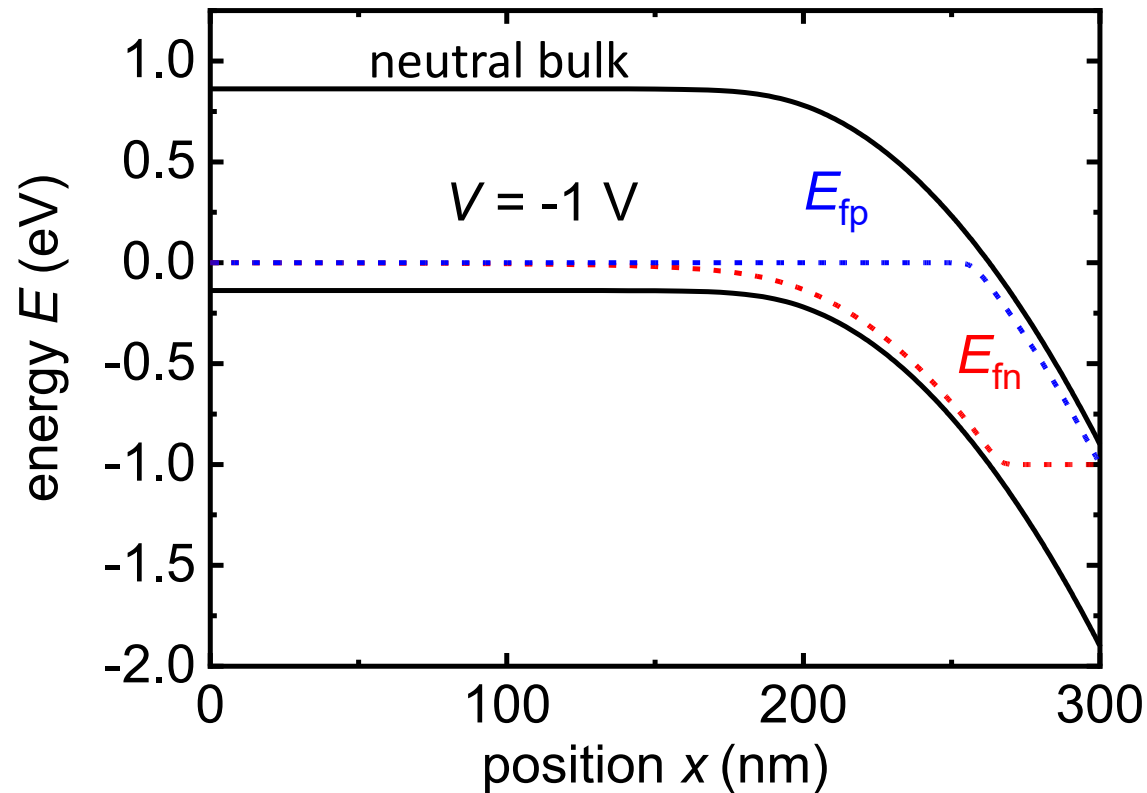


depletion layer capacitance

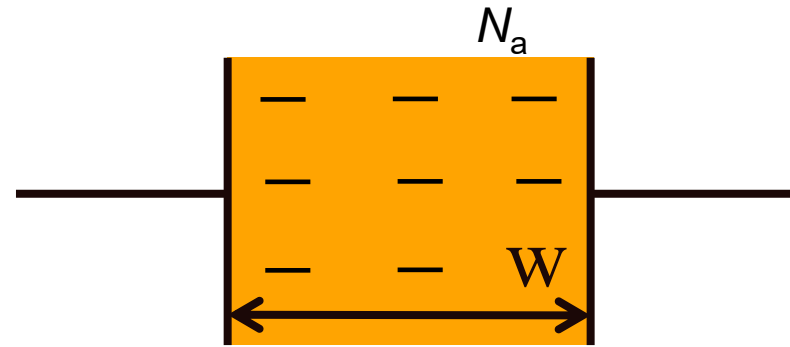
density of negatively-charged dopants N_a (cm^{-3})



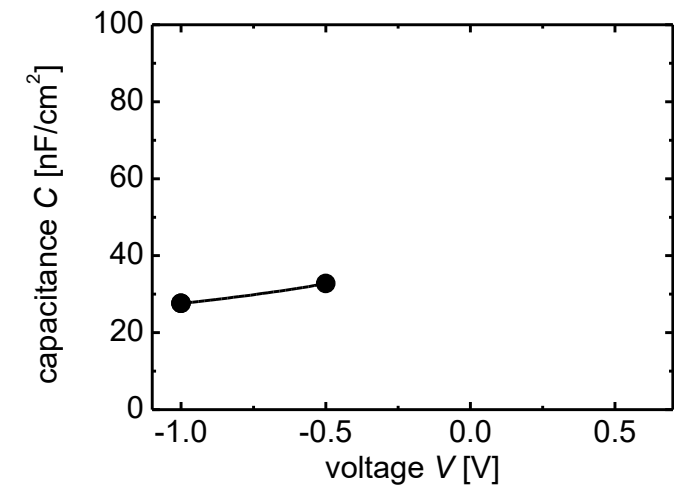
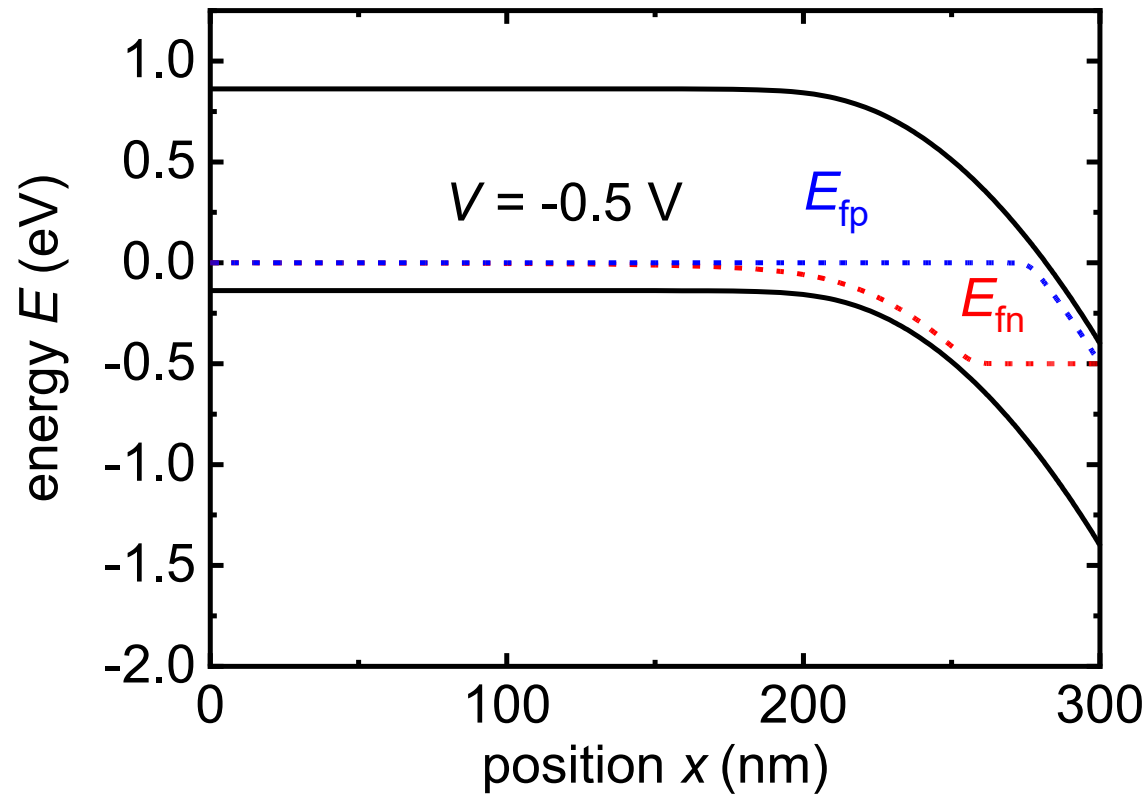
$$C = \frac{\epsilon_r \epsilon_0}{W}$$



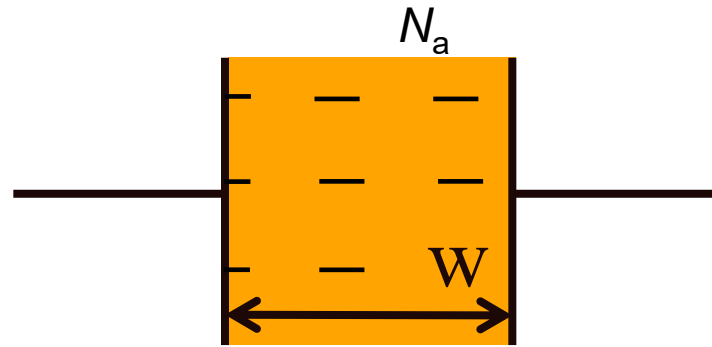
depletion layer capacitance



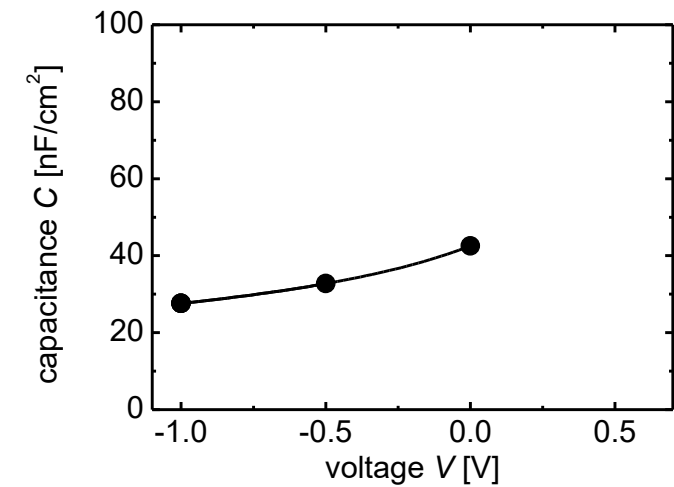
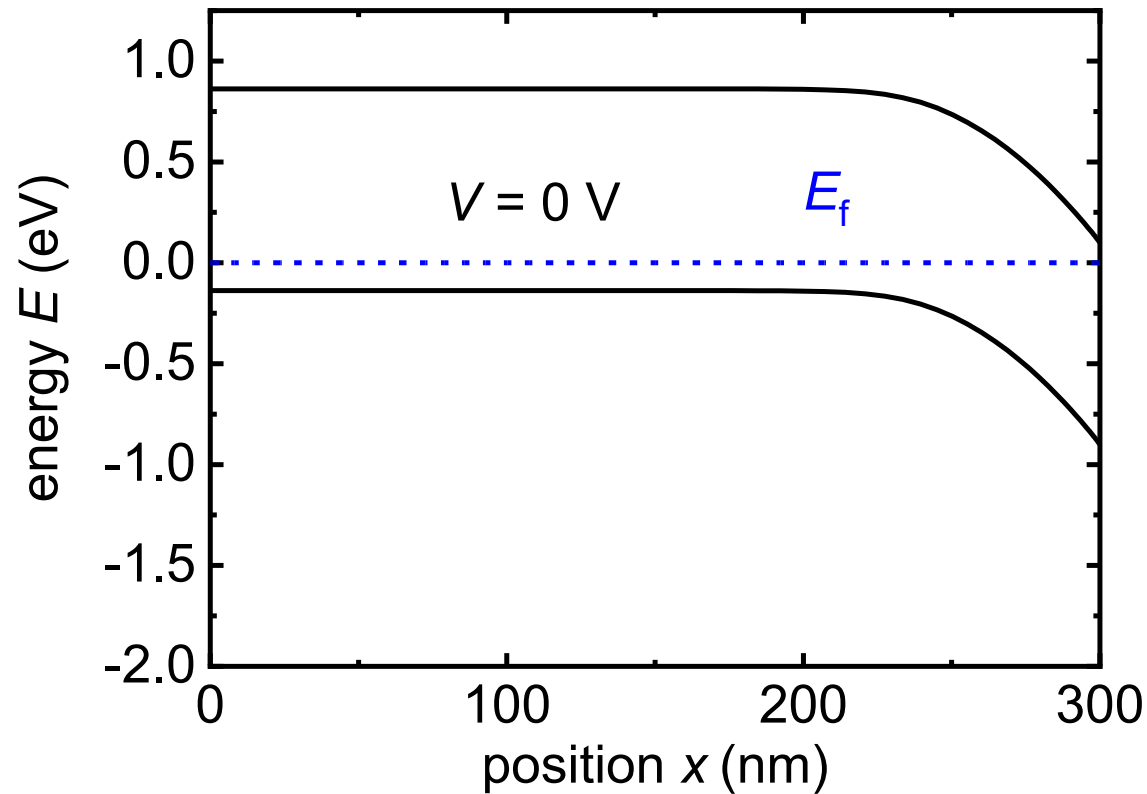
$$C = \frac{\epsilon_r \epsilon_0}{W}$$



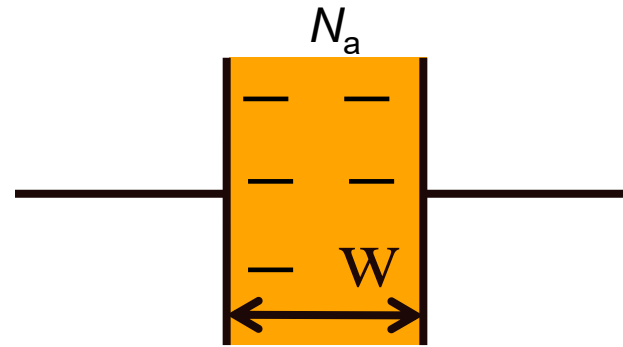
depletion layer capacitance



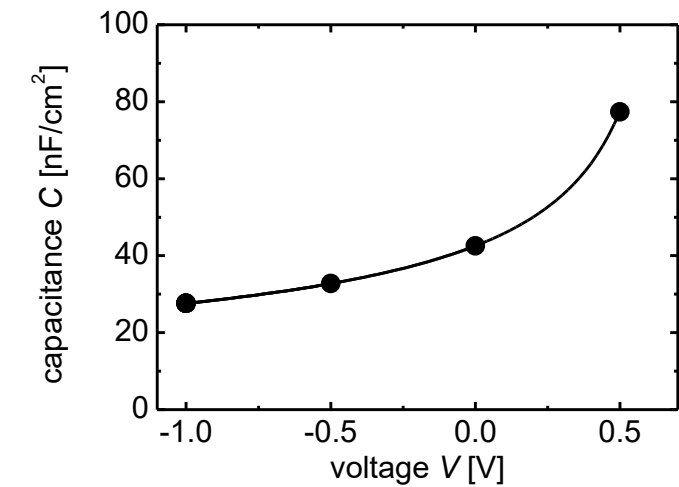
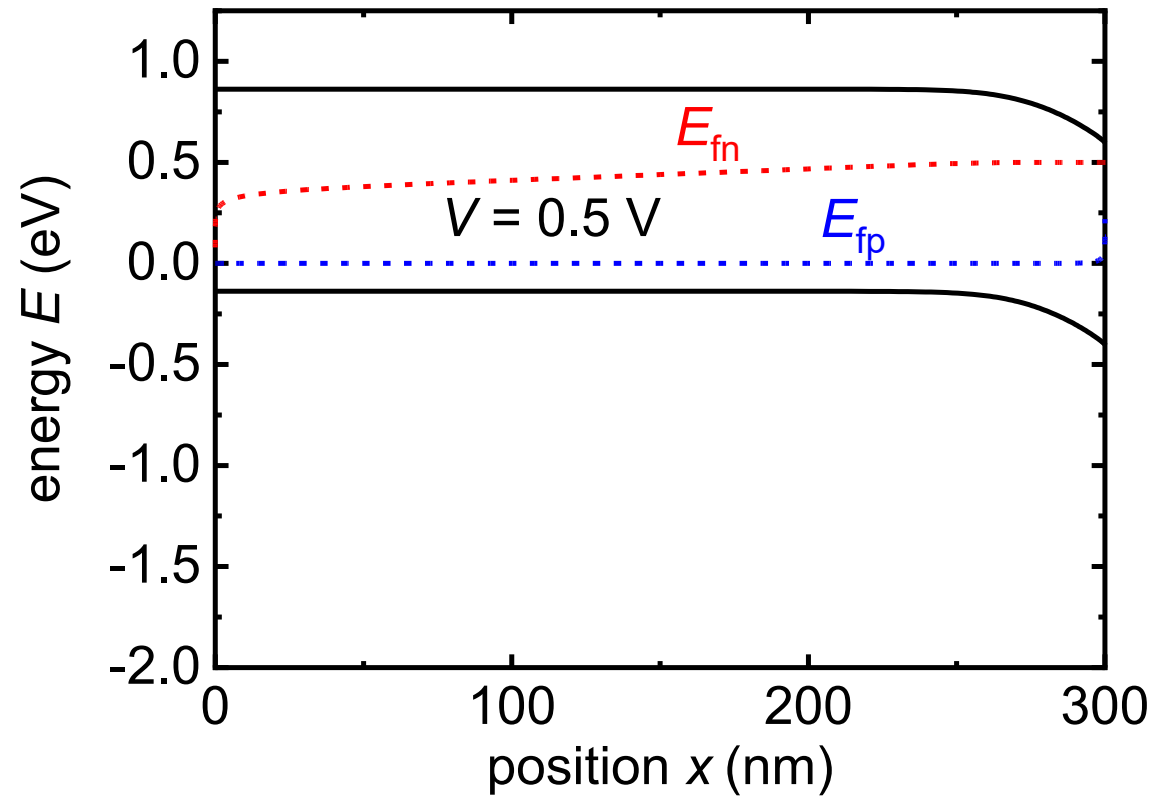
$$C = \frac{\epsilon_r \epsilon_0}{W}$$



depletion layer capacitance



$$C = \frac{\epsilon_r \epsilon_0}{W}$$

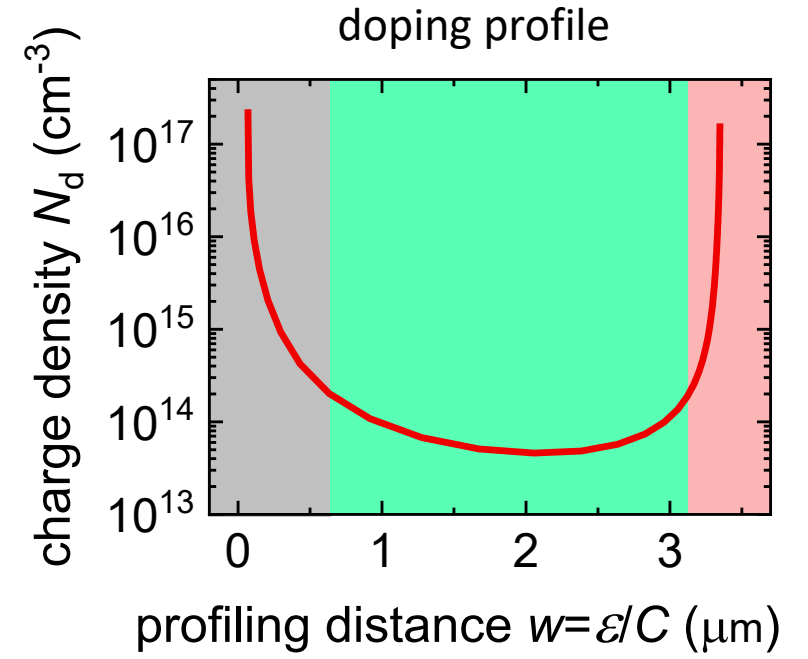
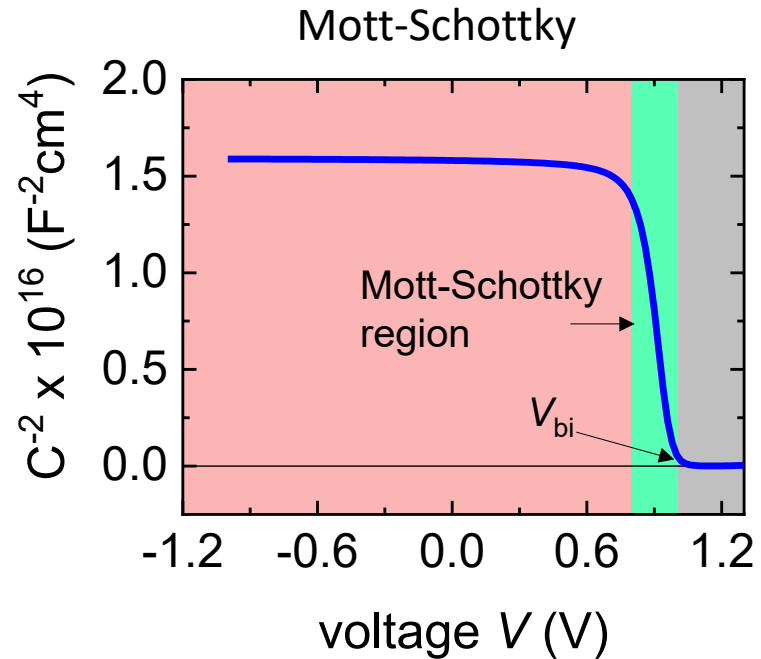
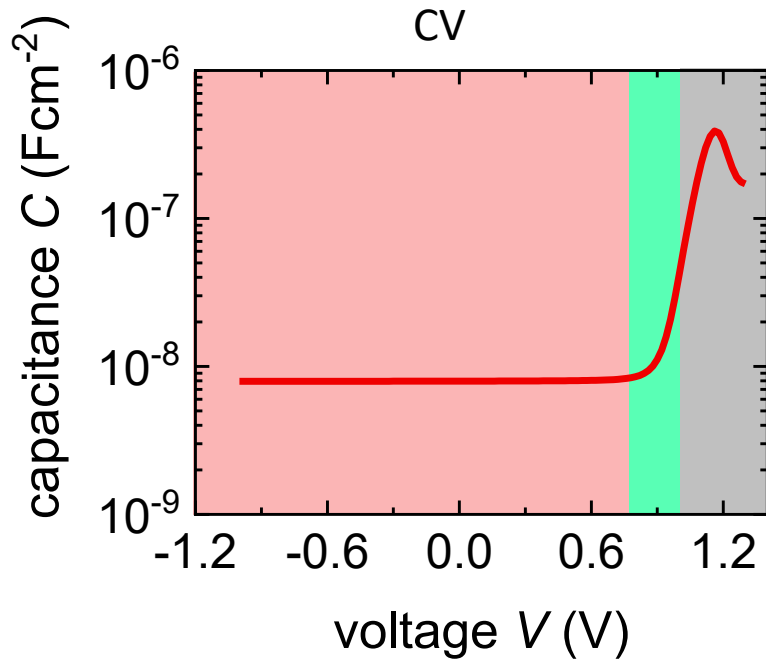


capacitance analysis

$$C(V) = \sqrt{\frac{q\epsilon_r\epsilon_0 N_d}{2(V_{bi} - V)}}$$

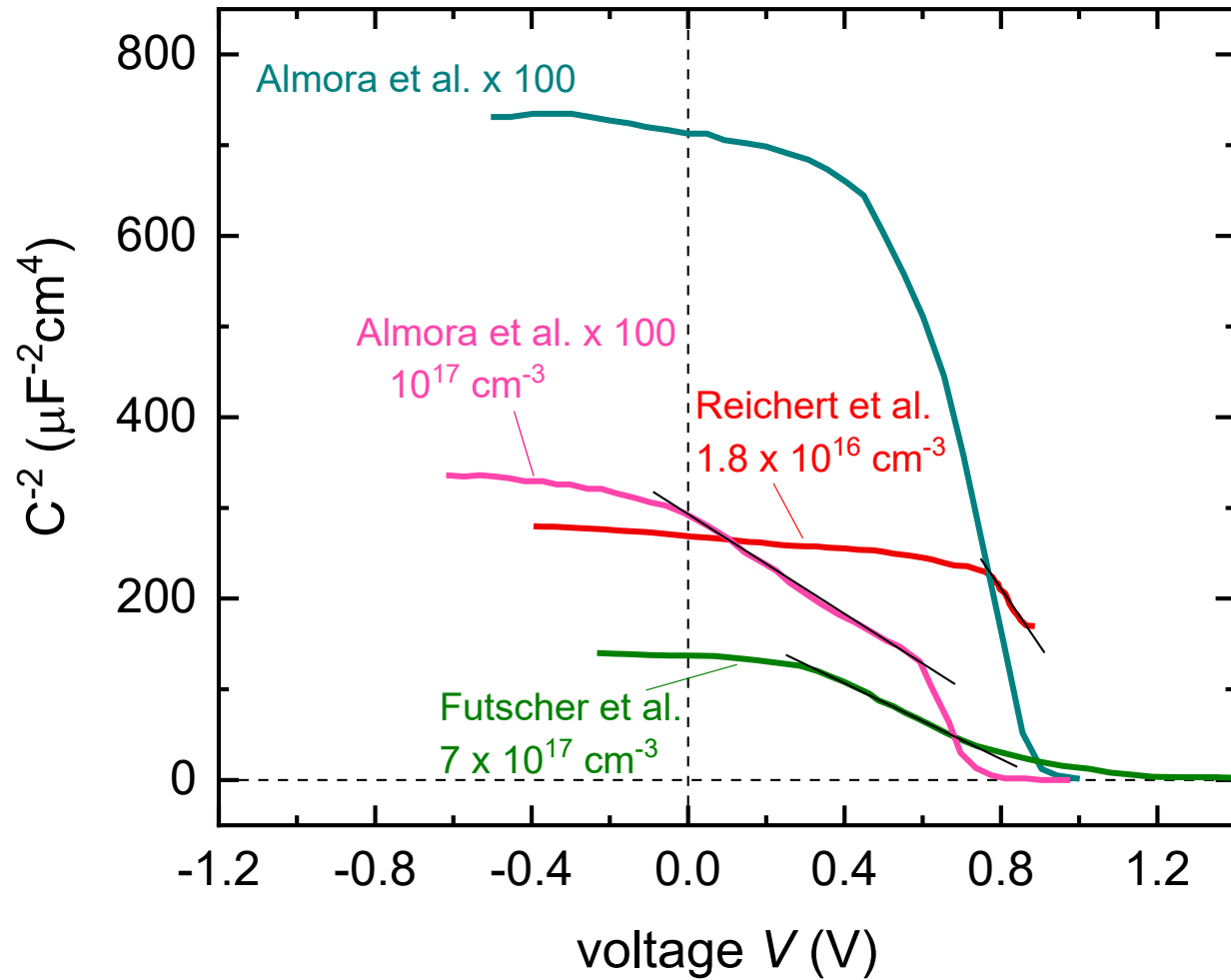
$$C^{-2}(V) = \frac{2}{q\epsilon_r\epsilon_0 N_d} (V_{bi} - V)$$

$$N_d(V) = \frac{-2(dC^{-2}/dV)^{-1}}{q\epsilon_r\epsilon_0}$$

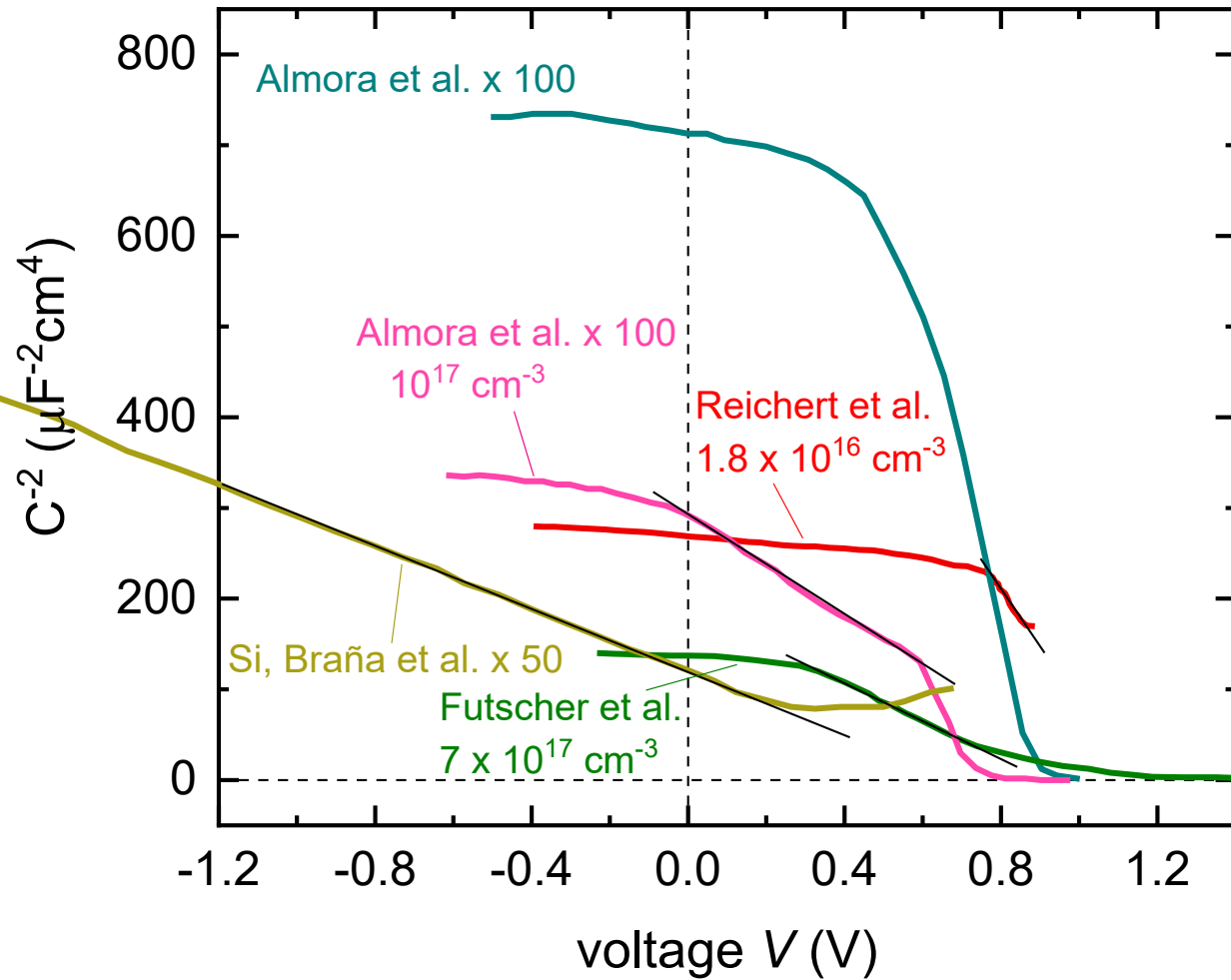


allows estimation of doping/defect density and built-in voltage

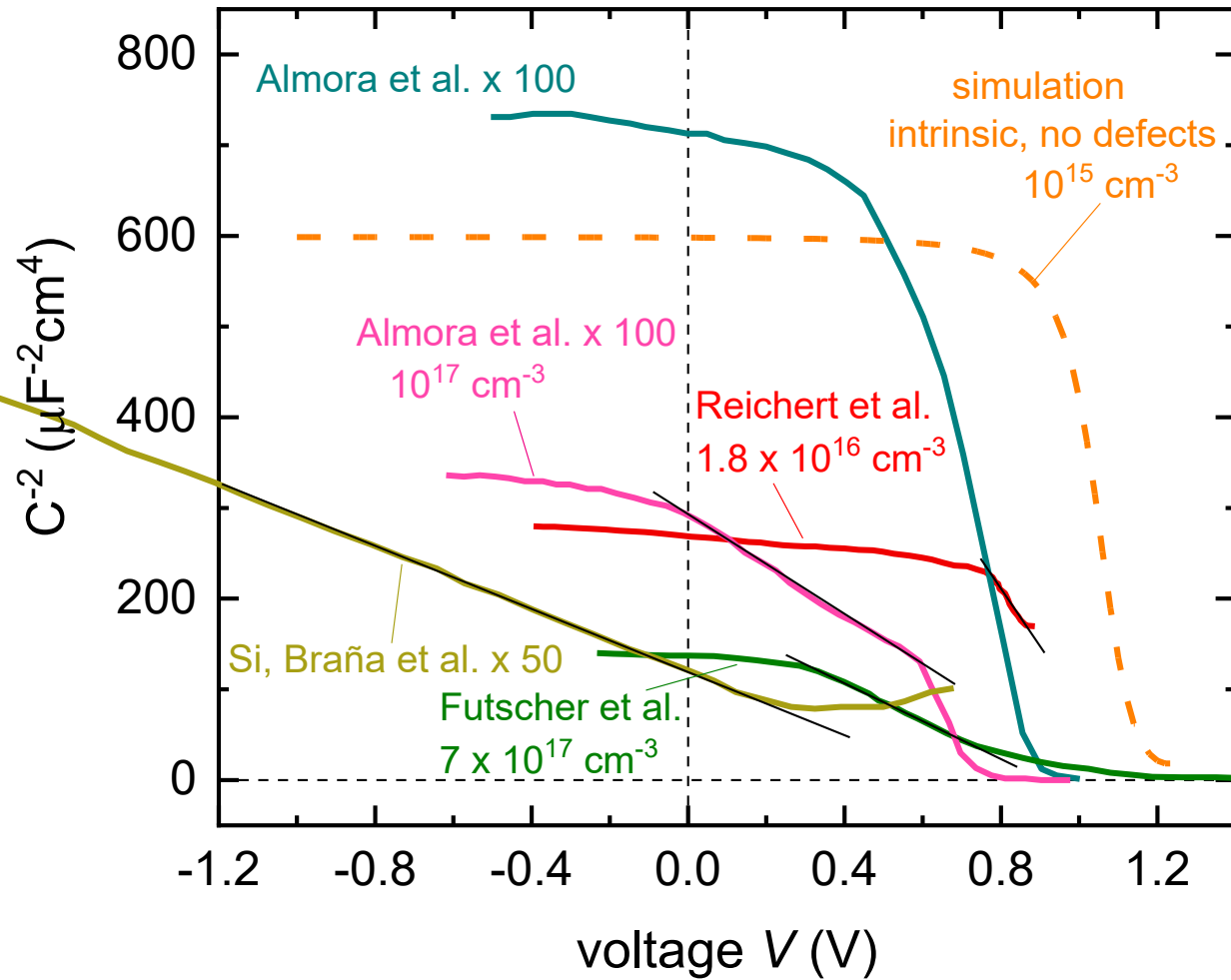
experimental Mott-Schottky plots



experimental Mott-Schottky plots

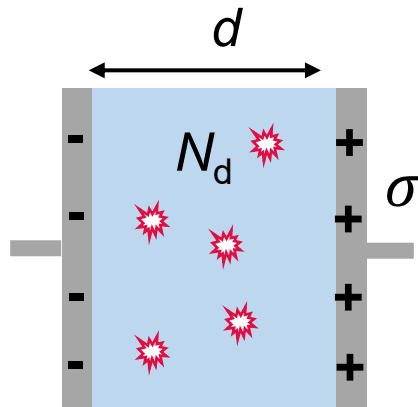


experimental Mott-Schottky plots



why does an intrinsic semiconductor make a Mott-Schottky behaviour?

competition between surface charge and bulk charge

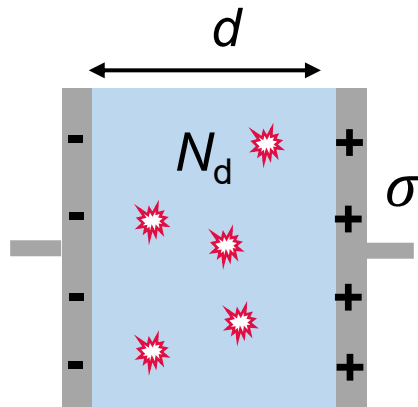


detection of a density of charged dopants/traps N_d requires

$$qdN_d \gg \sigma$$

volume charge surface charge

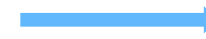
competition between surface charge and bulk charge



detection of a density of charged dopants/traps N_d requires

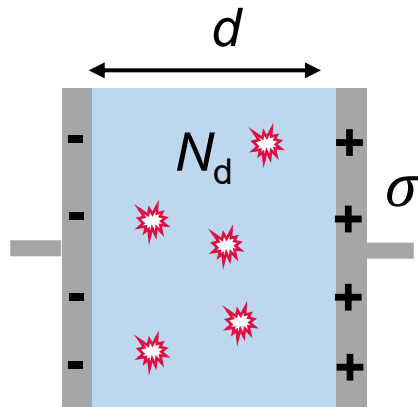
$$qdN_d \gg \sigma$$

volume charge surface charge



$$N_d \gg \frac{\epsilon V_{bi}}{qd^2}$$

competition between surface charge and bulk charge

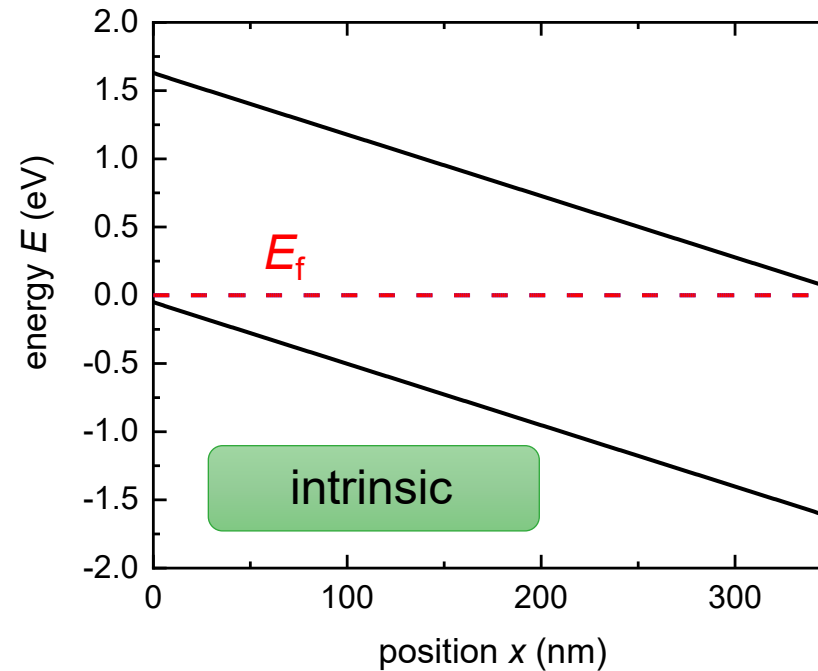


detection of a density of charged dopants/traps N_d requires

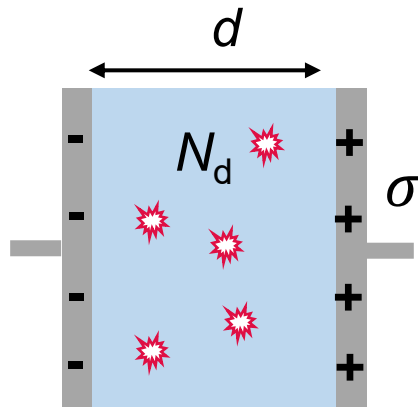
$$qdN_d \gg \sigma$$

volume charge \gg surface charge

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competition between surface charge and bulk charge

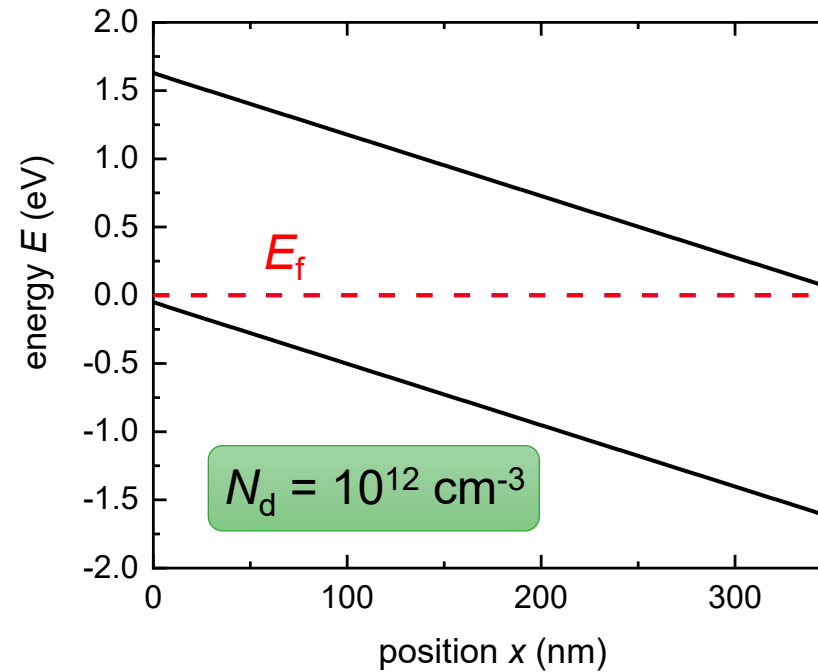


detection of a density of charged dopants/traps N_d requires

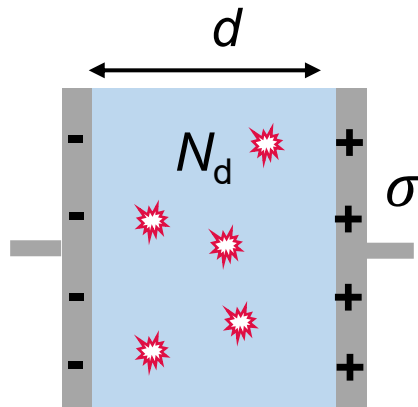
$$qdN_d \gg \sigma$$

volume charge \gg surface charge

$$N_d \gg \frac{\epsilon V_{bi}}{qd^2}$$



competition between surface charge and bulk charge

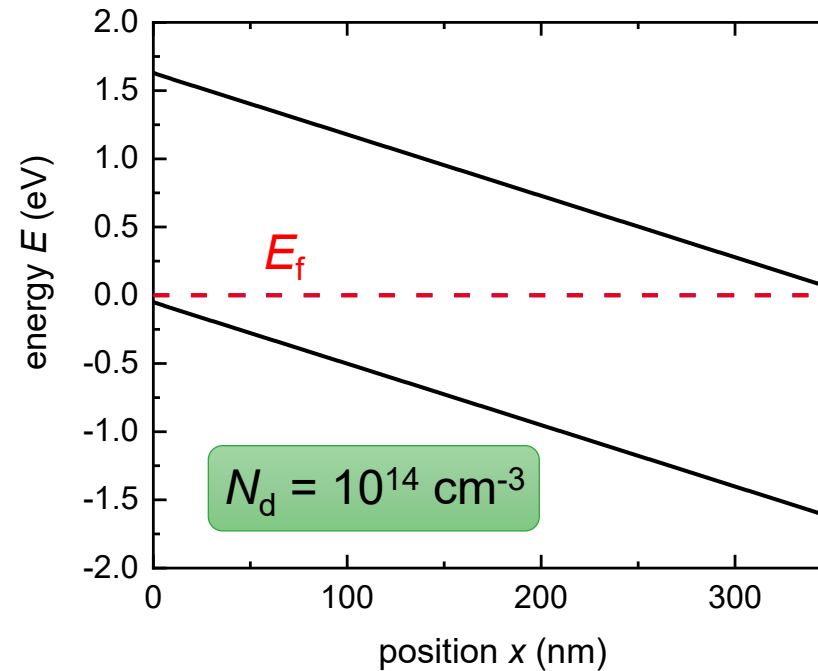


detection of a density of charged dopants/traps N_d requires

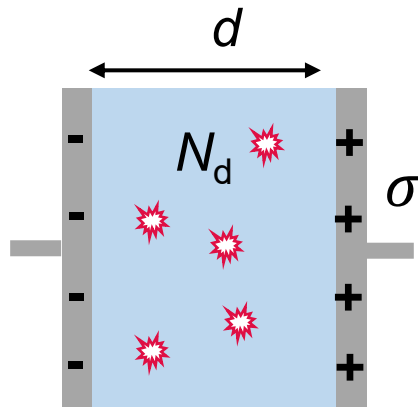
$$qdN_d \gg \sigma$$

volume charge \gg surface charge

$$N_d \gg \frac{\epsilon V_{bi}}{qd^2}$$



competition between surface charge and bulk charge

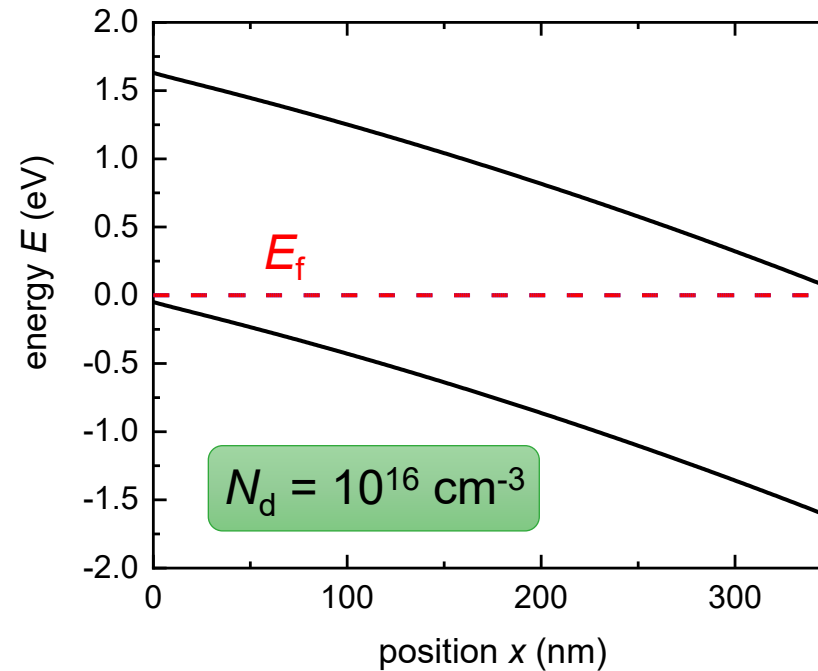


detection of a density of charged dopants/traps N_d requires

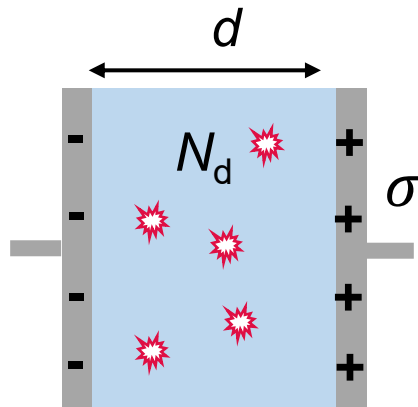
$$qdN_d \gg \sigma$$

volume charge \gg surface charge

$$N_d \gg \frac{\epsilon V_{bi}}{qd^2}$$



competition between surface charge and bulk charge

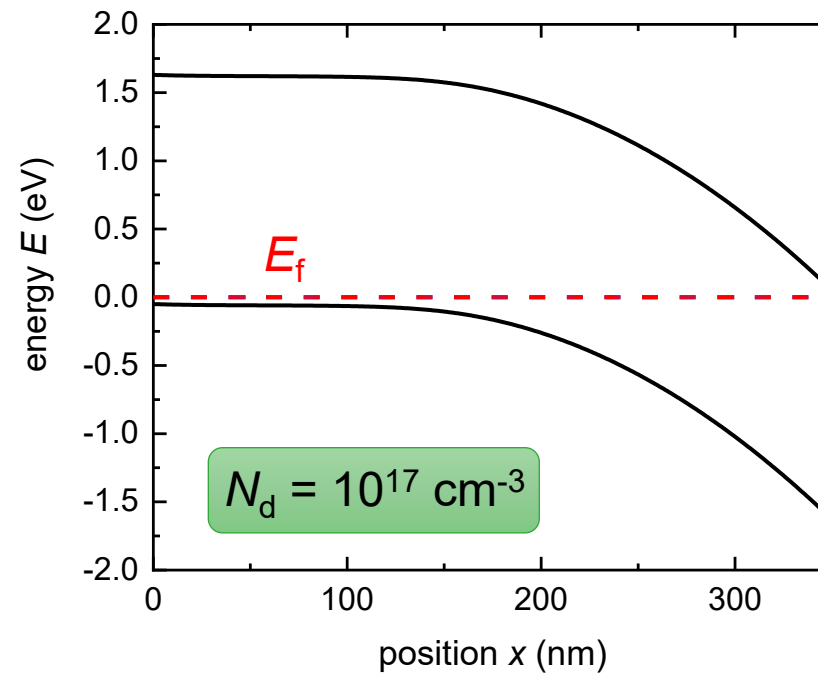


detection of a density of charged dopants/traps N_d requires

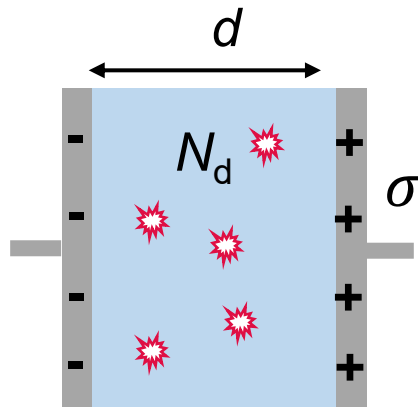
$$qdN_d \gg \sigma$$

volume charge \gg surface charge

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competition between surface charge and bulk charge

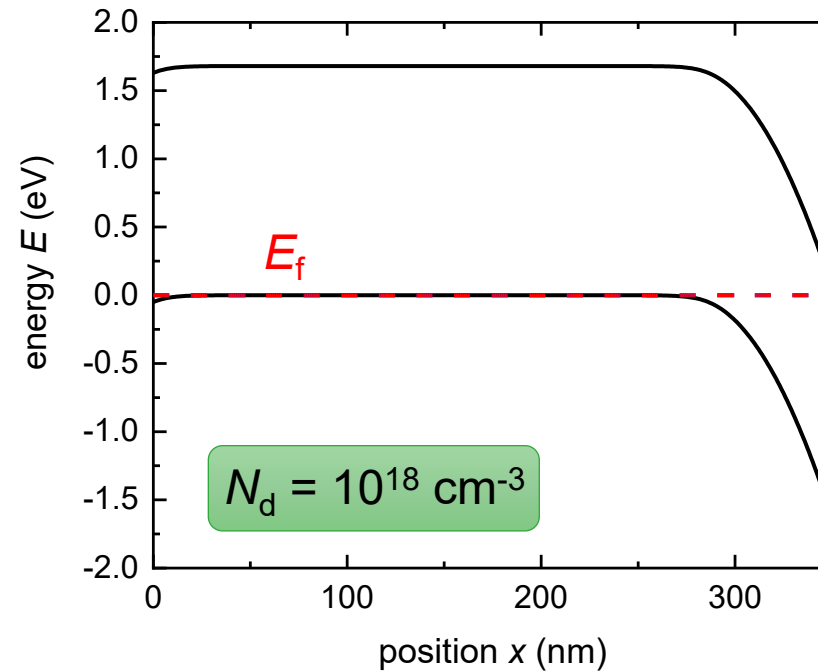


detection of a density of charged dopants/traps N_d requires

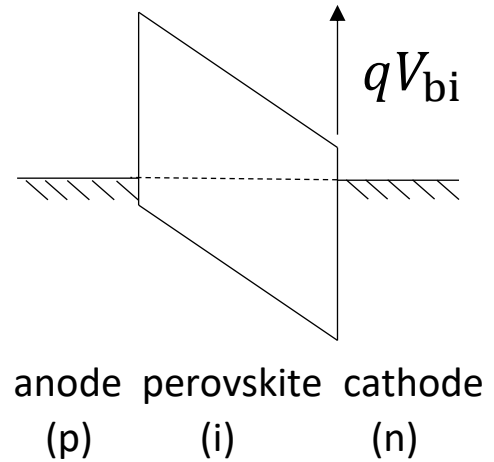
$$qdN_d \gg \sigma$$

volume charge \gg surface charge

$$N_d \gg \frac{\epsilon V_{bi}}{qd^2}$$

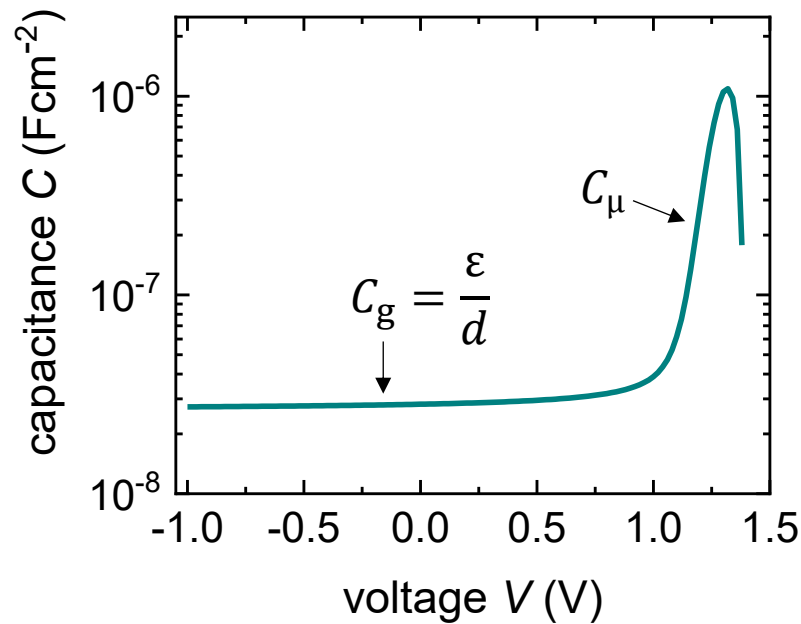
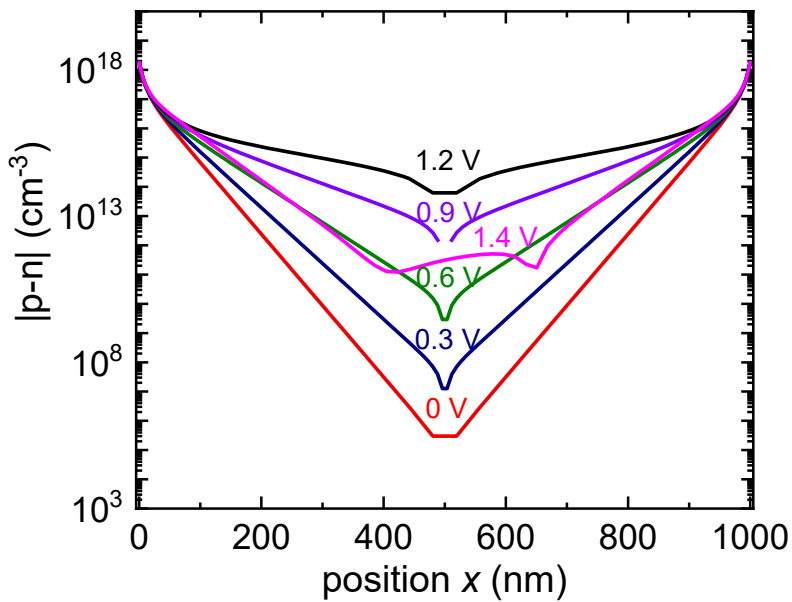


charge injection at forward bias

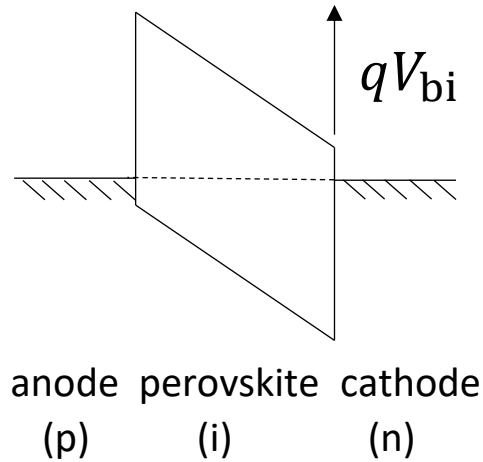


chemical capacitance

$$C_{\mu} = C_0 \exp \frac{qV}{m_{CV} k_B T}$$

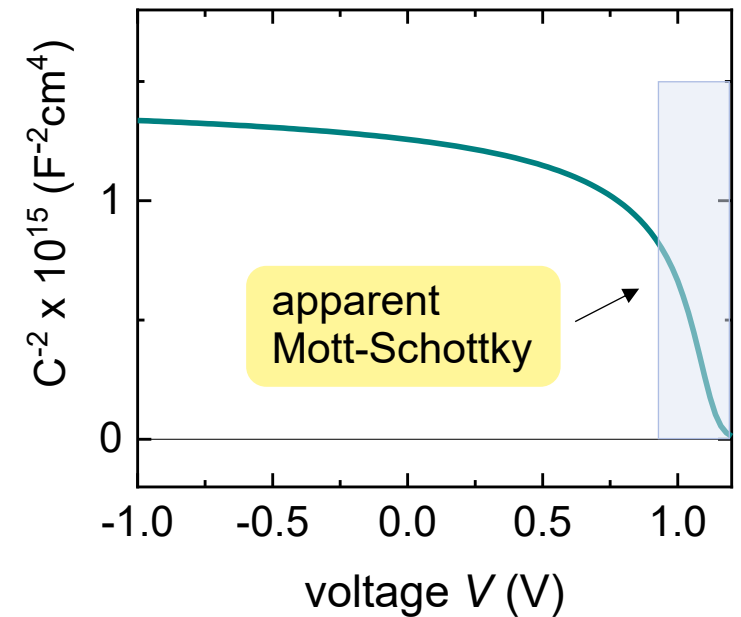
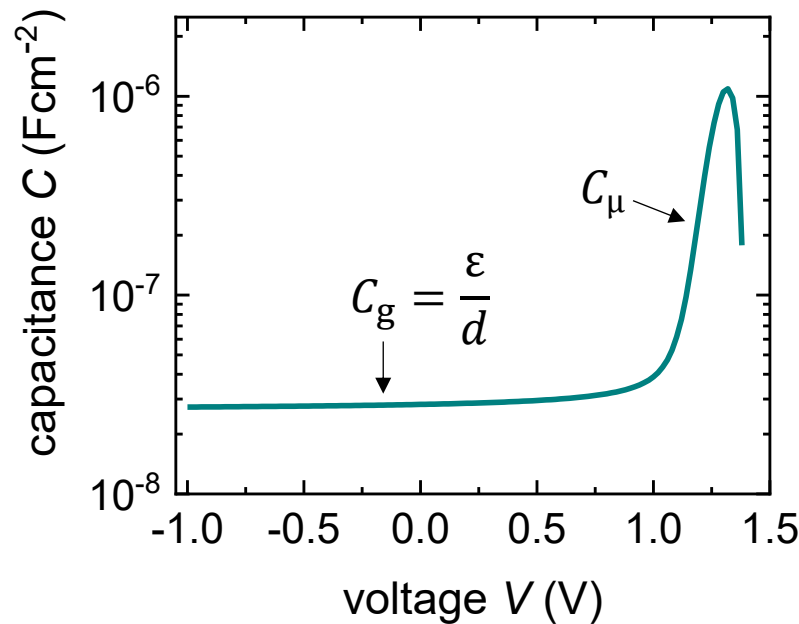
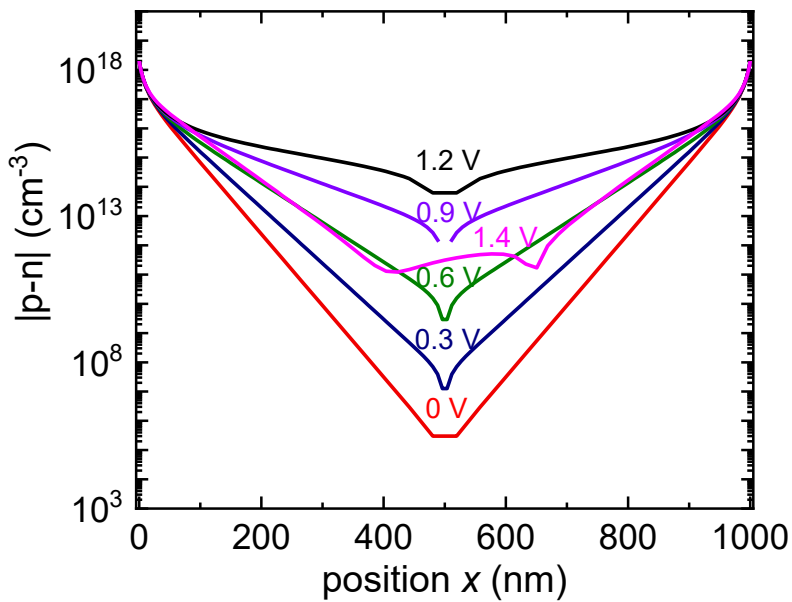


charge injection at forward bias



chemical capacitance

$$C_{\mu} = C_0 \exp \frac{qV}{m_{CV} k_B T}$$



key question

can we resolve doping and defect densities from overlapping mechanisms in capacitance measurements?

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$$C(V) = C_g + C_0 \exp \frac{qV}{m_{CV} k_B T}$$

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$$C(V) = C_g + C_0 \exp \frac{qV}{m_{CV} k_B T}$$



$$N_d(V) = \frac{-2}{q \epsilon_r \epsilon_0} \left(\frac{dC^{-2}}{dV} \right)^{-1}$$

can we resolve doping and defect densities from overlapping mechanisms in capacitance measurements?

$$C(V) = C_g + C_0 \exp \frac{qV}{m_{CV} k_B T}$$



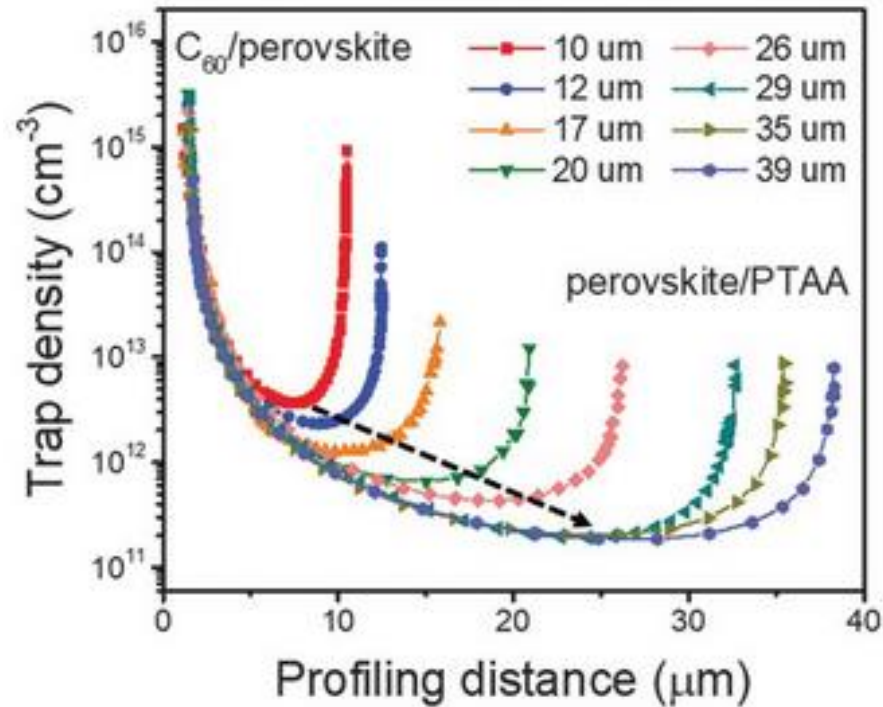
$$N_d(V) = \frac{-2}{q \epsilon_r \epsilon_0} \left(\frac{dC^{-2}}{dV} \right)^{-1}$$



$$N_{d,\min} = \frac{27 m_{CV} k_B T \epsilon_r \epsilon_0}{4 q^2 d^2}$$

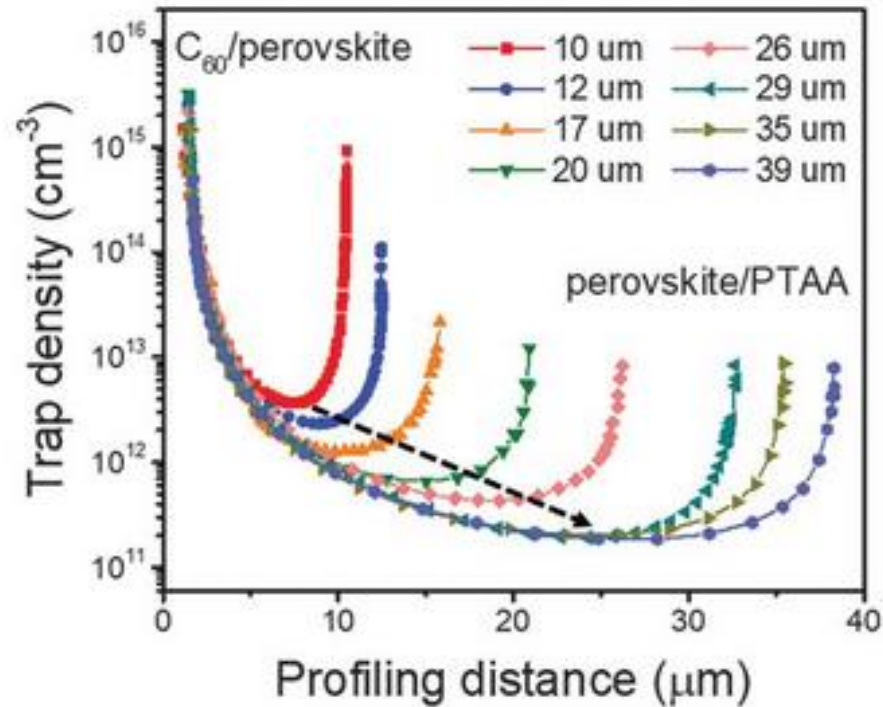
minimum defect or doping density resolvable in a capacitance measurement

drive-level capacitance profiling (DLCP)

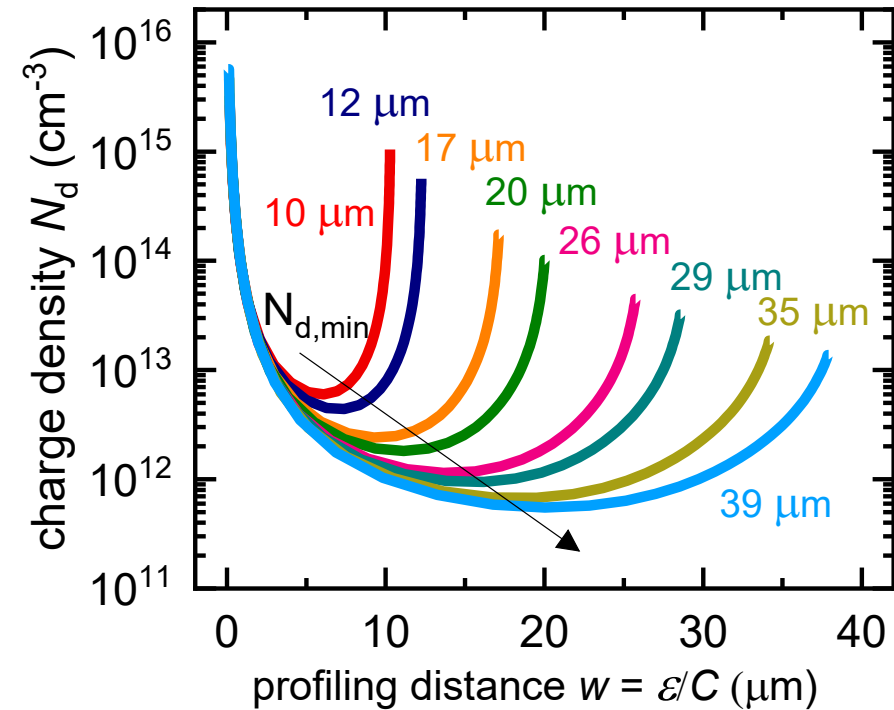


| Perovskite material | Minimal bulk trap density ($N_{T \min}$) (cm^{-3}) | Interface trap density (cm^{-3}) | |
|---|---|---|---|
| MAPbBr ₃ single crystal (bulk) | 6.5×10^{10} | 1.8×10^{12} (C ₆₀) | 1.8×10^{12} (Au) |
| MAPbI ₃ single crystal (bulk) | 1.8×10^{11} | 1.2×10^{12} (C ₆₀) | 1.2×10^{12} (Au) |
| MAPbI ₃ single crystal (thin) | 1.9×10^{11} to 3.2×10^{12} | 2.0×10^{13} to 1.1×10^{16} (C ₆₀) | 1.5×10^{13} to 1.0×10^{15} (PTAA) |
| Cs _{0.05} FA _{0.70} MA _{0.25} PbI ₃ film | 4.3×10^{14} | 8.6×10^{15} (C ₆₀) | 1.2×10^{17} (PTAA) |
| Rb _{0.05} Cs _{0.05} FA _{0.75} MA _{0.15} Pb(I _{0.95} Br _{0.05}) ₃ film | 5.7×10^{14} | 2.0×10^{16} (C ₆₀) | 1.1×10^{17} (PTAA) |
| FA _{0.92} MA _{0.08} PbI ₃ film | 7.9×10^{14} | 1.9×10^{16} (C ₆₀) | 9.0×10^{16} (PTAA) |
| MAPbI ₃ film | 9.2×10^{14} | 2.2×10^{16} (C ₆₀) | 1.2×10^{17} (PTAA) |
| Cs _{0.05} FA _{0.8} MA _{0.15} Pb _{0.5} Sn _{0.5} (I _{0.85} Br _{0.15}) ₃ film | 1.2×10^{15} | 1.5×10^{16} (C ₆₀) | 1.1×10^{17} (PTAA) |

drive-level capacitance profiling (DLCP)

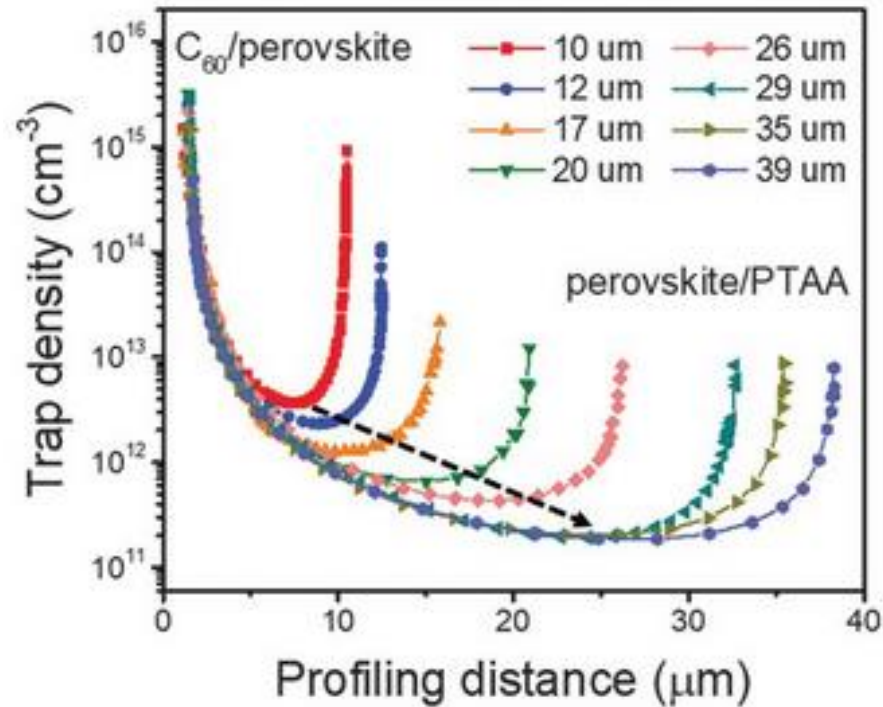


simulation: dopant-and-trap-free PSC

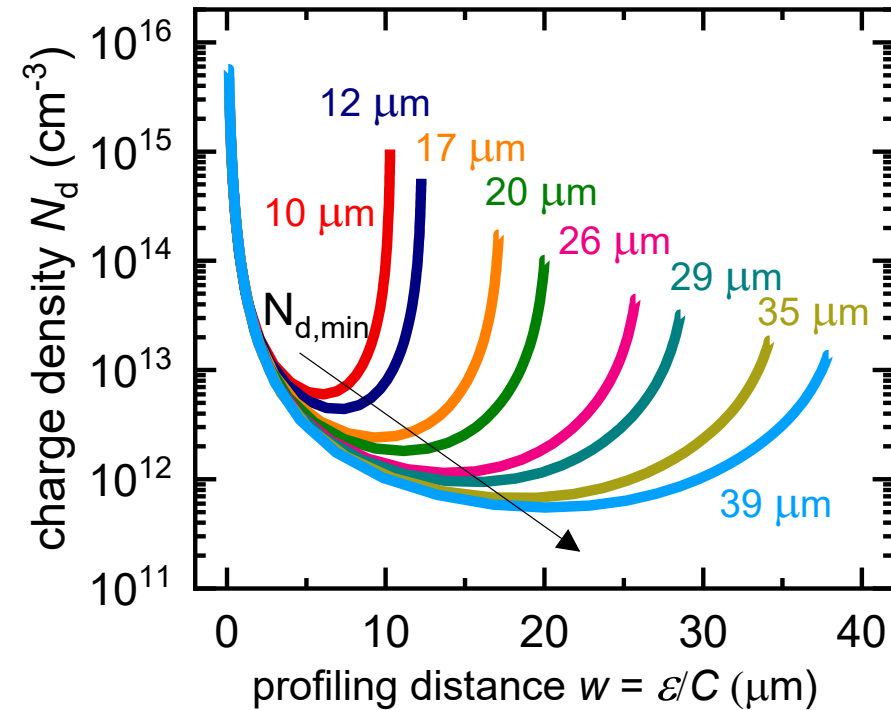


| Perovskite material | Minimal bulk trap density ($N_{T, min}$) (cm^{-3}) | Interface trap density (cm^{-3}) | |
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| MAPbBr ₃ single crystal (bulk) | 6.5×10^{10} | 1.8×10^{12} (C_{60}) | 1.8×10^{12} (Au) |
| MAPbI ₃ single crystal (bulk) | 1.8×10^{11} | 1.2×10^{12} (C_{60}) | 1.2×10^{12} (Au) |
| MAPbI ₃ single crystal (thin) | 1.9×10^{11} to 3.2×10^{12} | 2.0×10^{13} to 1.1×10^{16} (C_{60}) | 1.5×10^{13} to 1.0×10^{15} (PTAA) |
| Cs _{0.05} FA _{0.70} MA _{0.25} PbI ₃ film | 4.3×10^{14} | 8.6×10^{15} (C_{60}) | 1.2×10^{17} (PTAA) |
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| Cs _{0.05} FA _{0.8} MA _{0.15} Pb _{0.5} Sn _{0.5} (I _{0.85} Br _{0.15}) ₃ film | 1.2×10^{15} | 1.5×10^{16} (C_{60}) | 1.1×10^{17} (PTAA) |

drive-level capacitance profiling (DLCP)

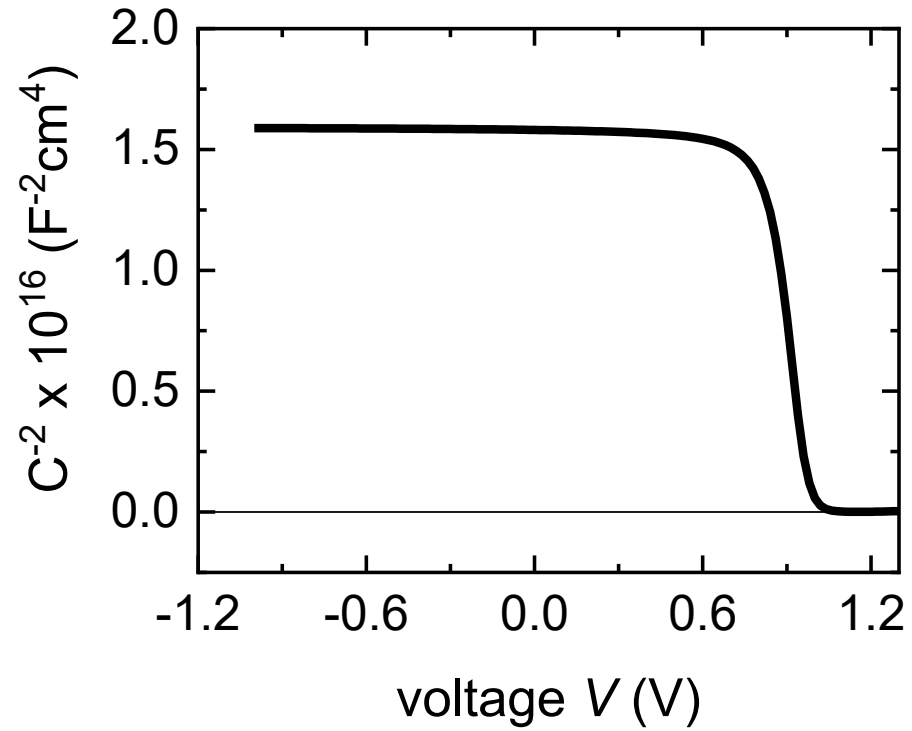


simulation: dopant-and-trap-free PSC



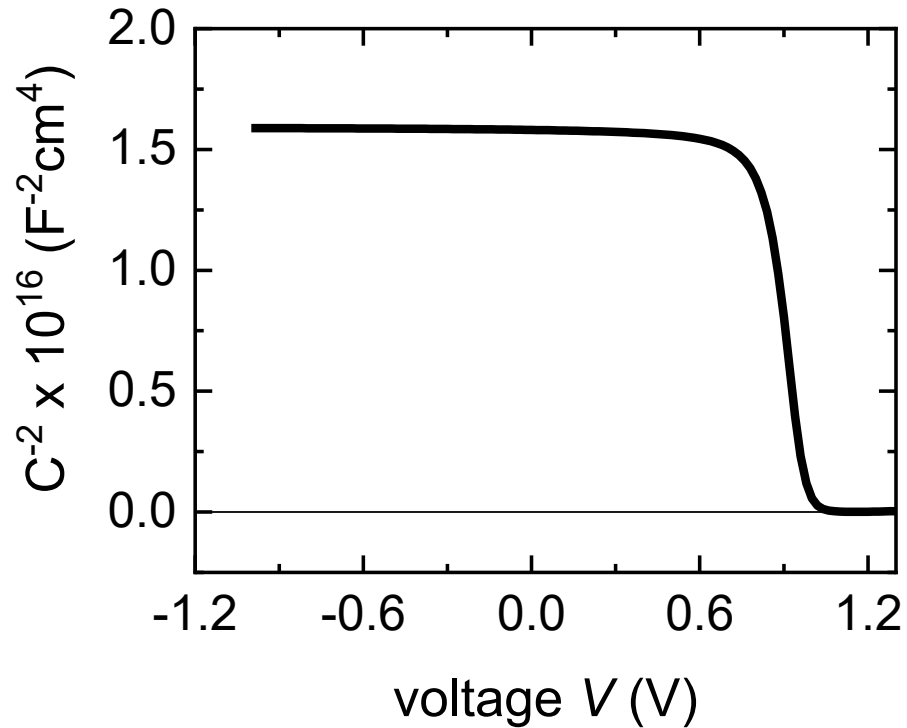
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| MAPbI ₃ single crystal (bulk) | 1.8×10^{11} | 1.2×10^{12} (C_{60}) | 1.2×10^{12} (Au) |
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| CS _{0.05} FA _{0.8} MA _{0.15} Pb _{0.5} Sn _{0.5} (I _{0.85} Br _{0.15}) ₃ film | 1.2×10^{15} | 1.5×10^{16} (C_{60}) | 1.1×10^{17} (PTAA) |

← NOT real defect densities

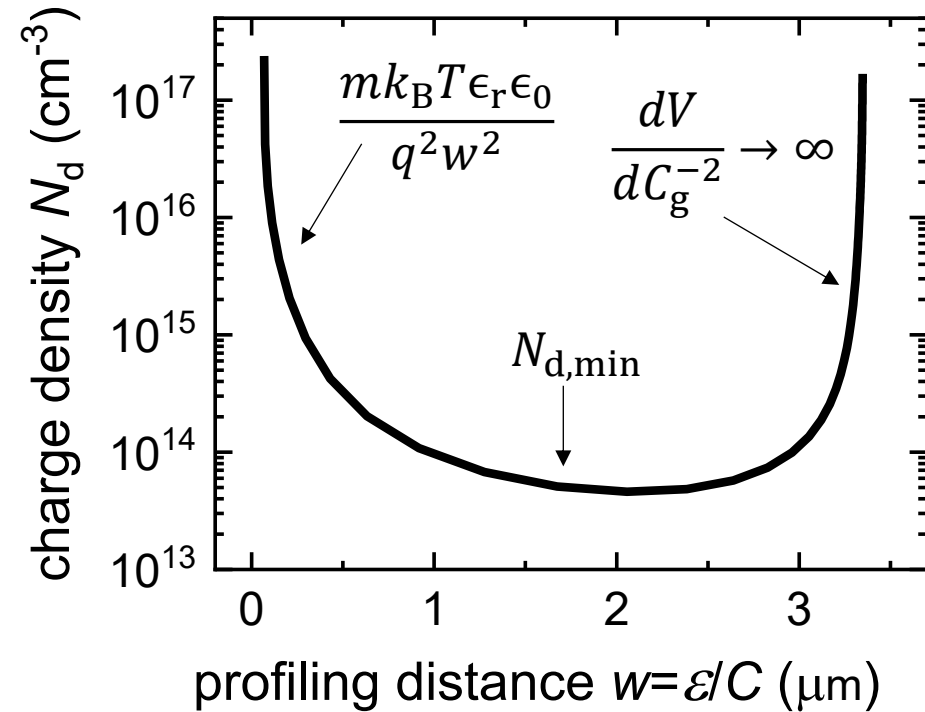


$$C(V) = C_g + C_0 \exp\left(\frac{qV}{mk_B T}\right)$$

analysis of doping profiles



$$\xrightarrow{(dC^{-2}/dV)^{-1}}$$



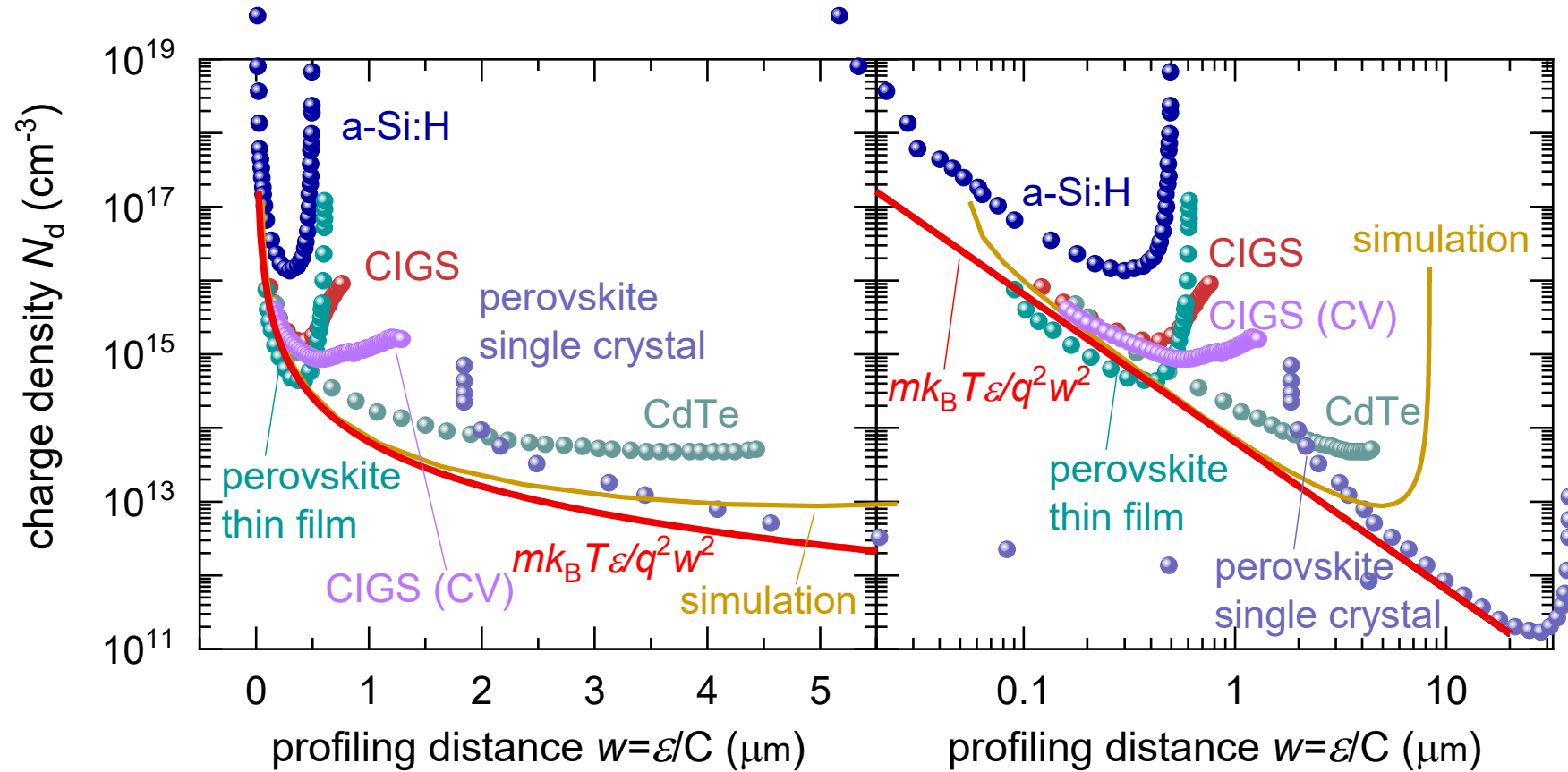
$$C(V) = C_g + C_0 \exp\left(\frac{qV}{mk_B T}\right)$$



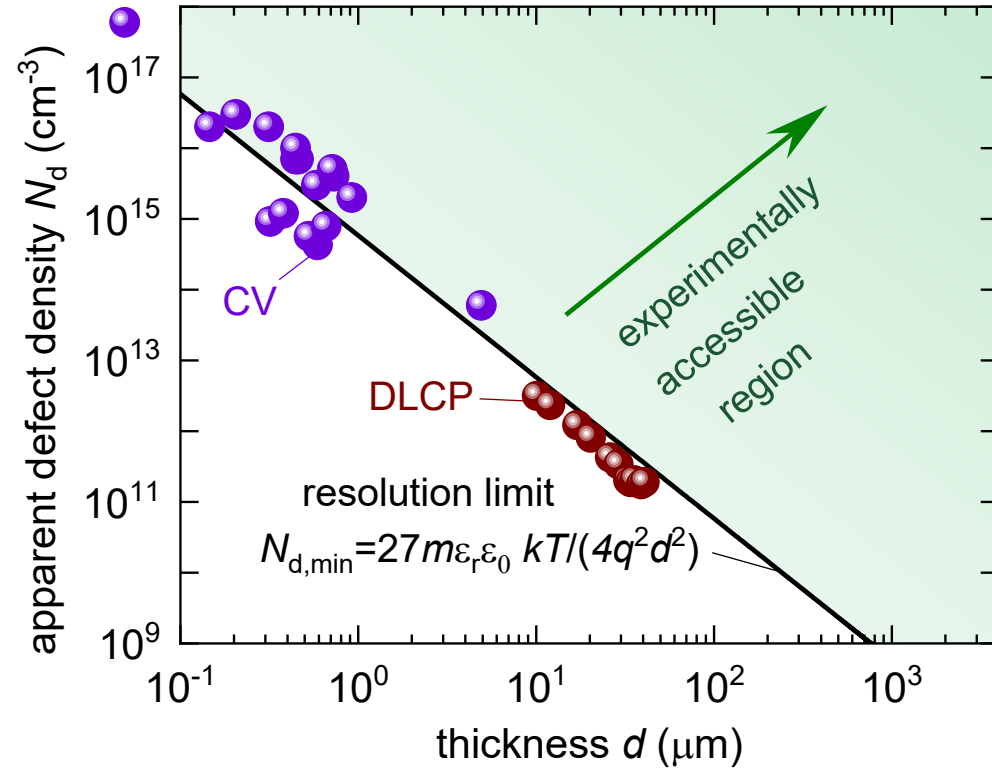
$$N_d(w) = N_{d,min} + \frac{mk_B T \epsilon_r \epsilon_0}{q^2 w^2}$$

apparent defect densities – infinite rise due to C_g , minimum determined by resolution limit

other photovoltaic technologies

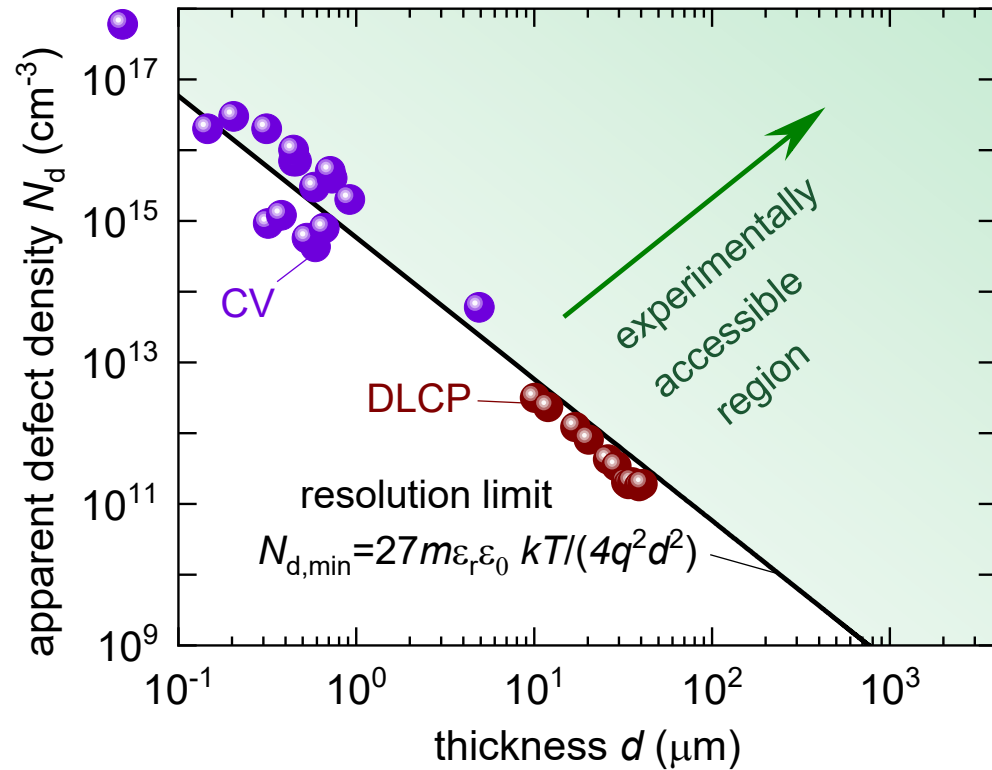


measured defect densities in literature

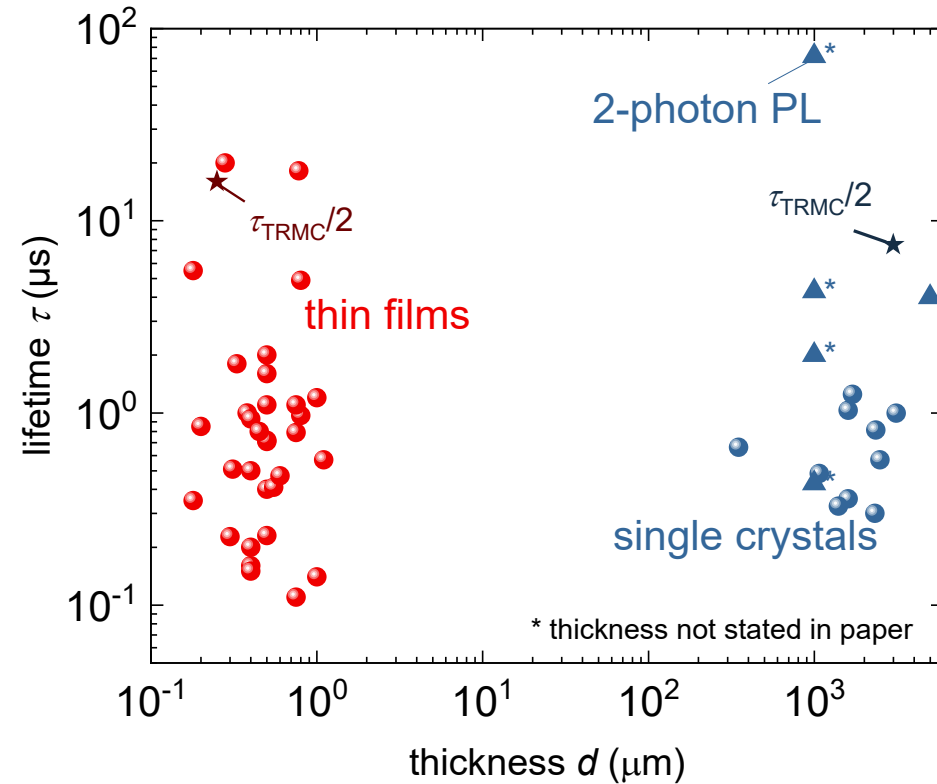


all apparent defect densities are close to the resolution limit

measured defect densities in literature

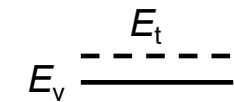
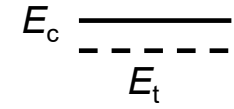
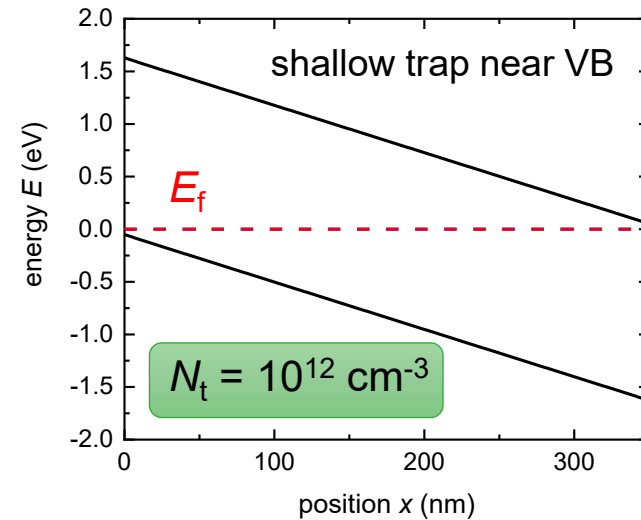
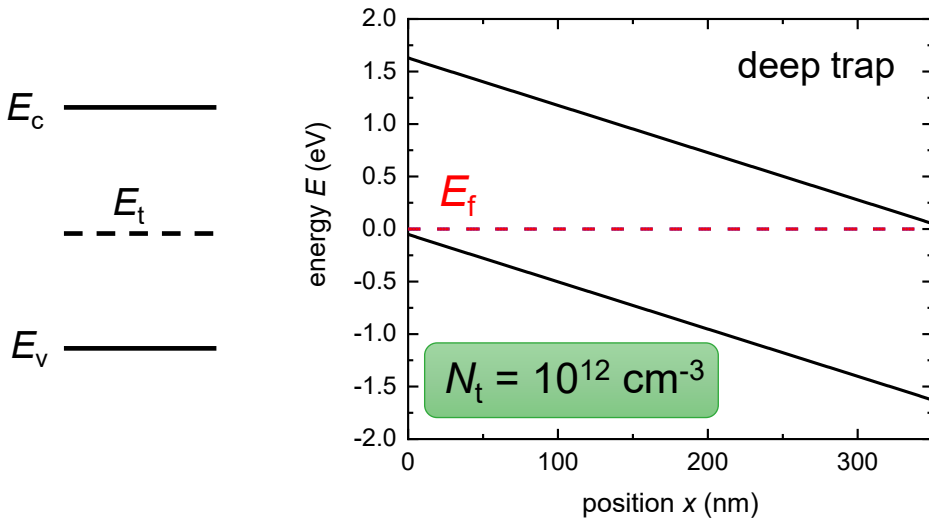
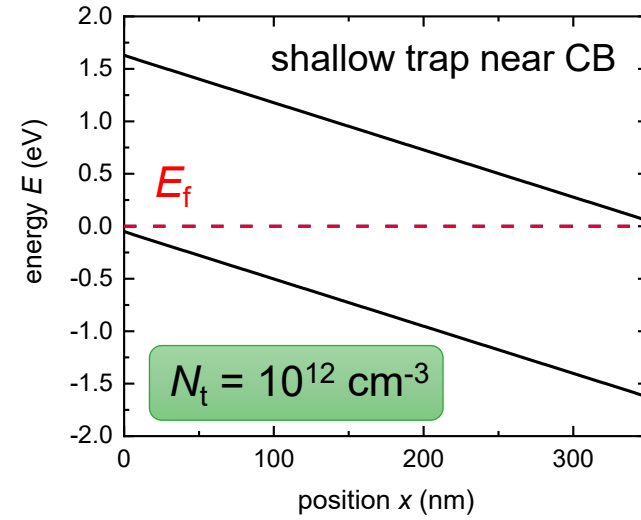
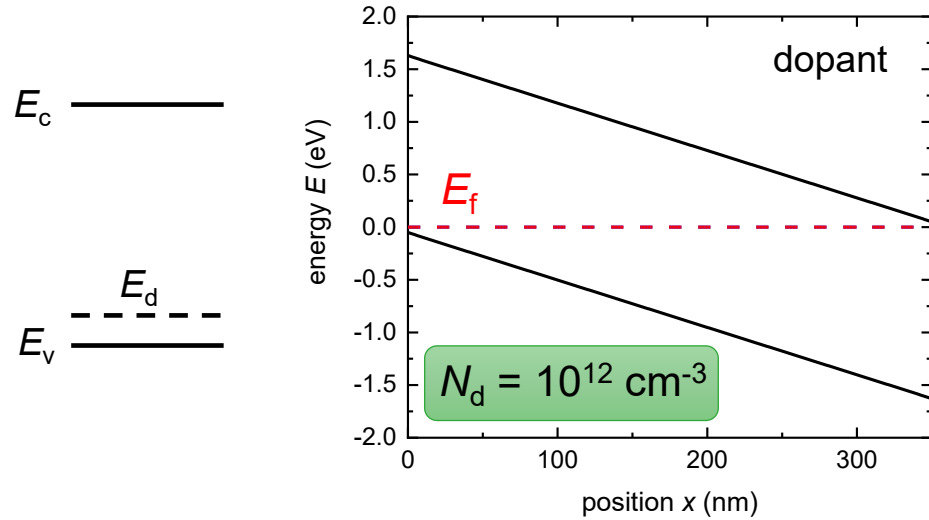


all apparent defect densities are close to the resolution limit

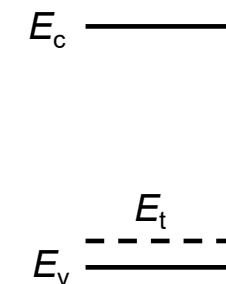
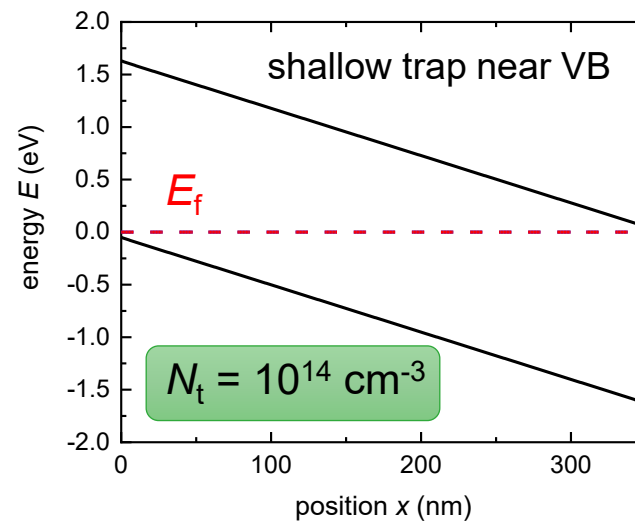
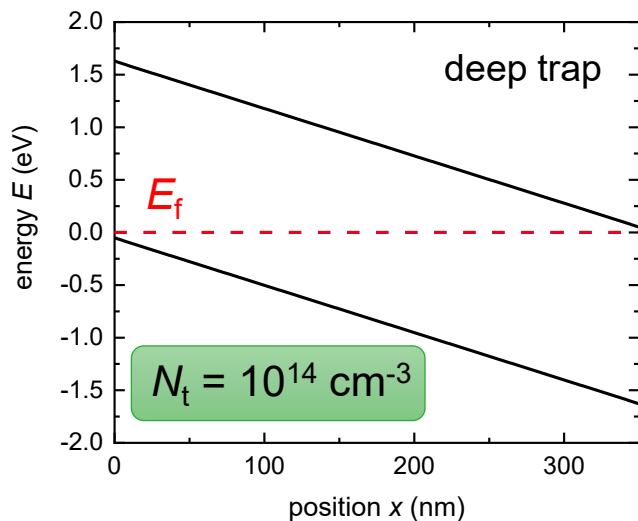
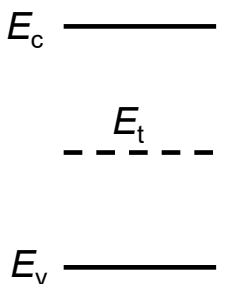
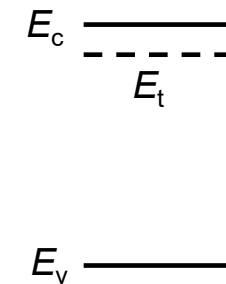
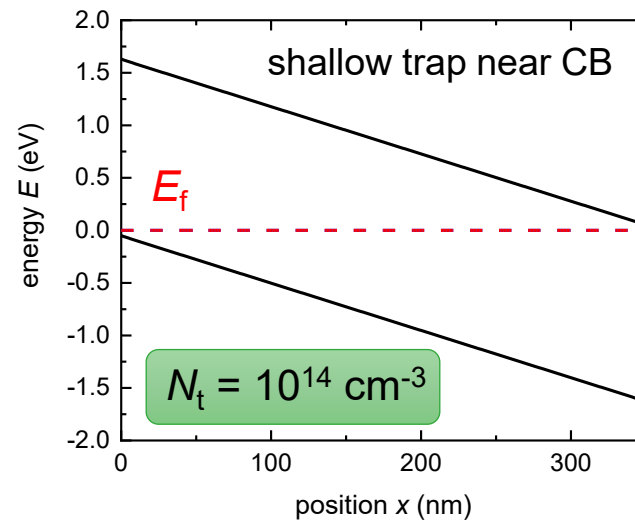
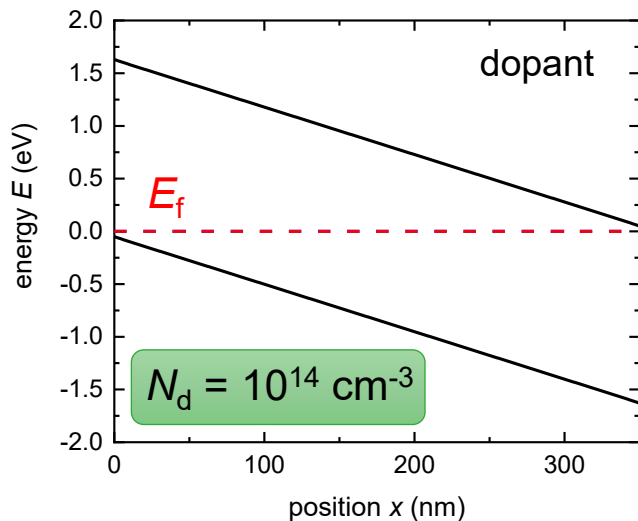
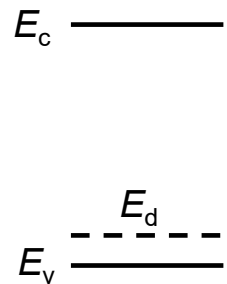


recombination lifetimes not correlated to apparent defect densities (ideally $\tau \propto \frac{1}{N_d}$)

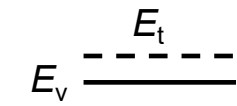
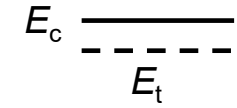
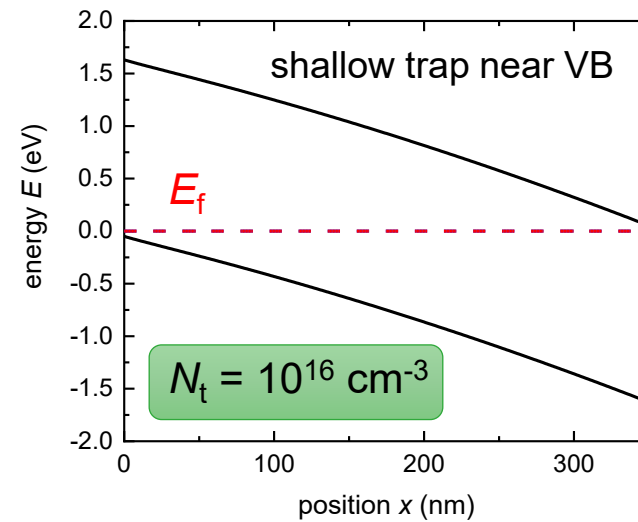
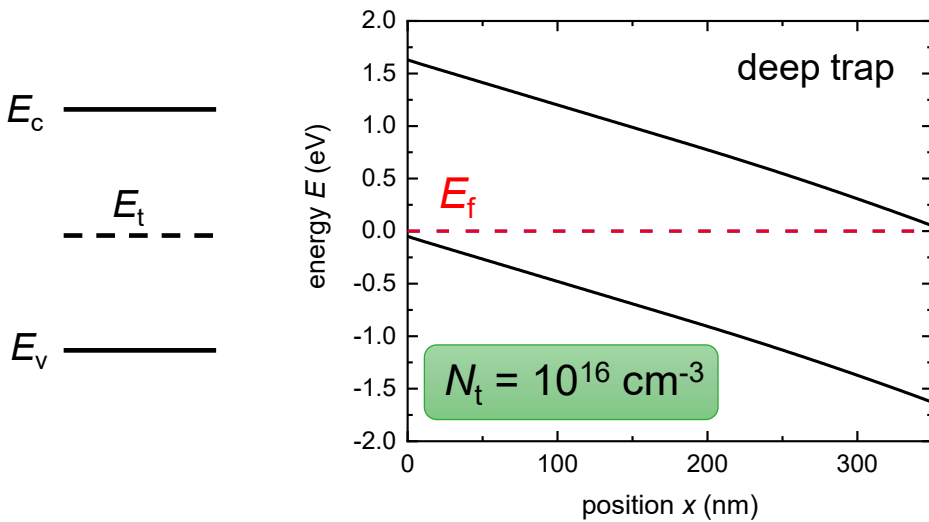
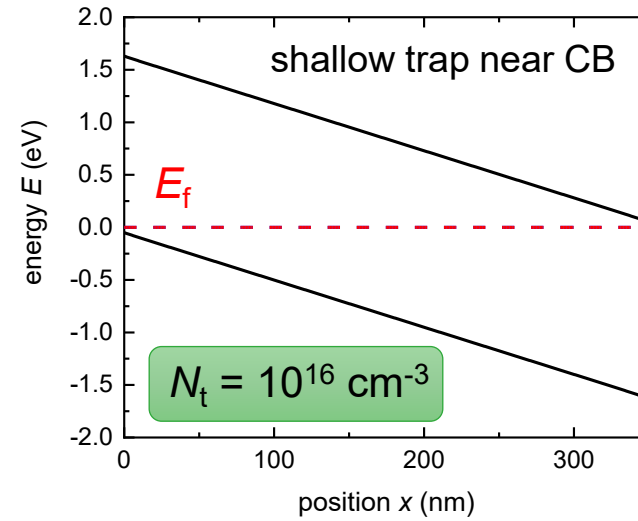
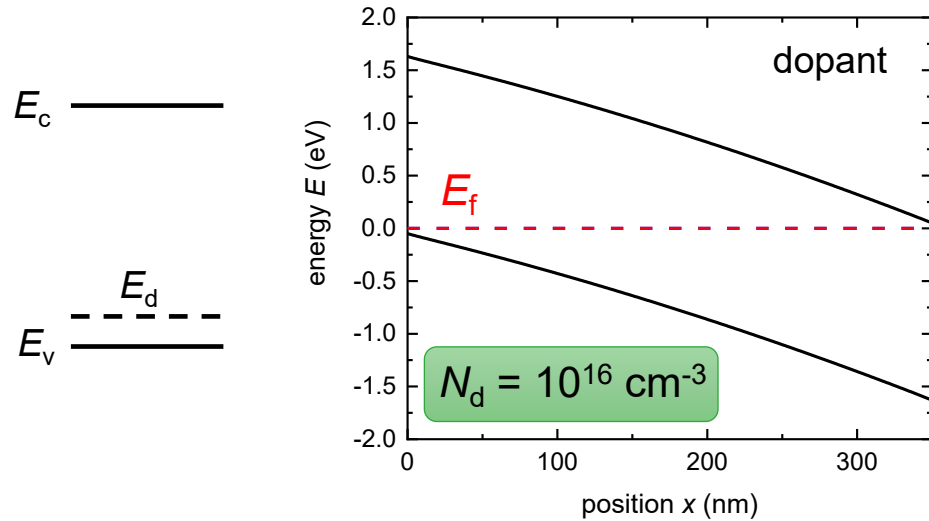
do dopants and defects have the same effect?



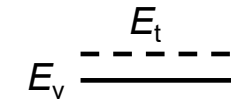
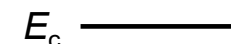
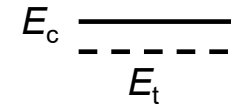
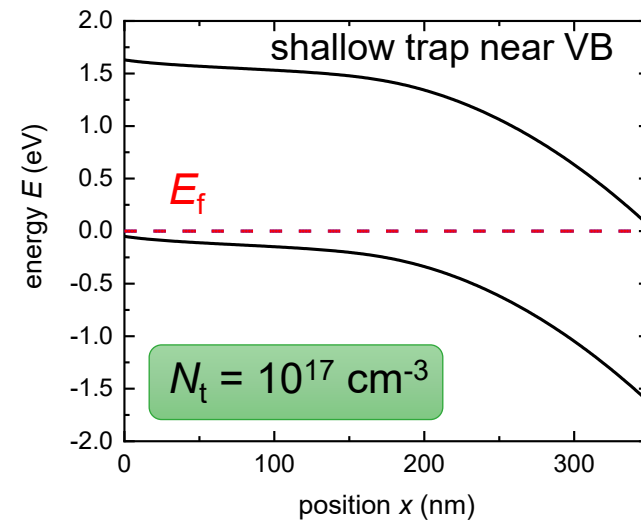
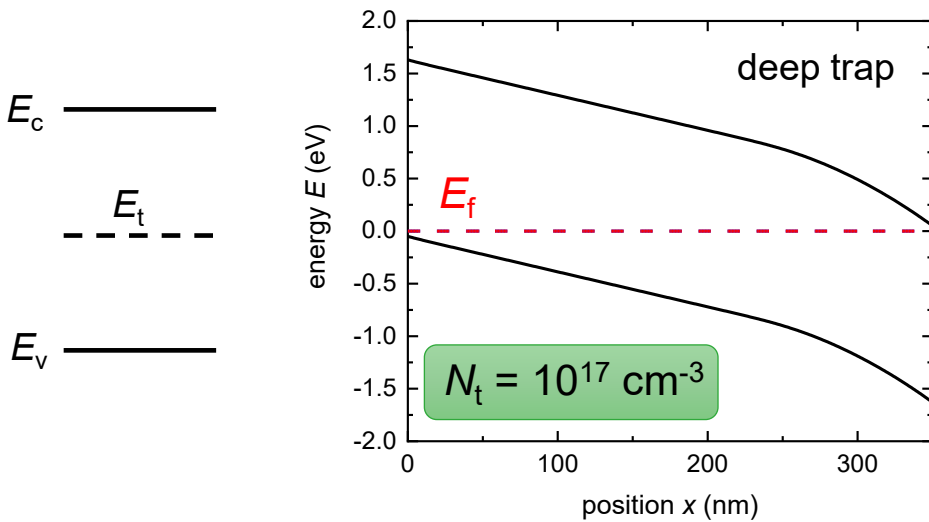
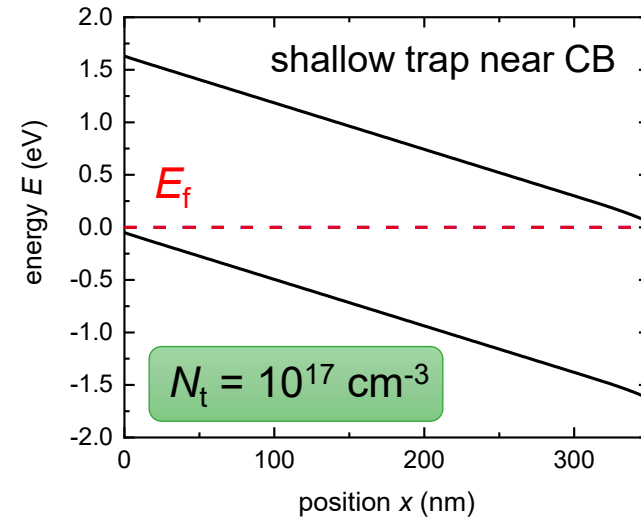
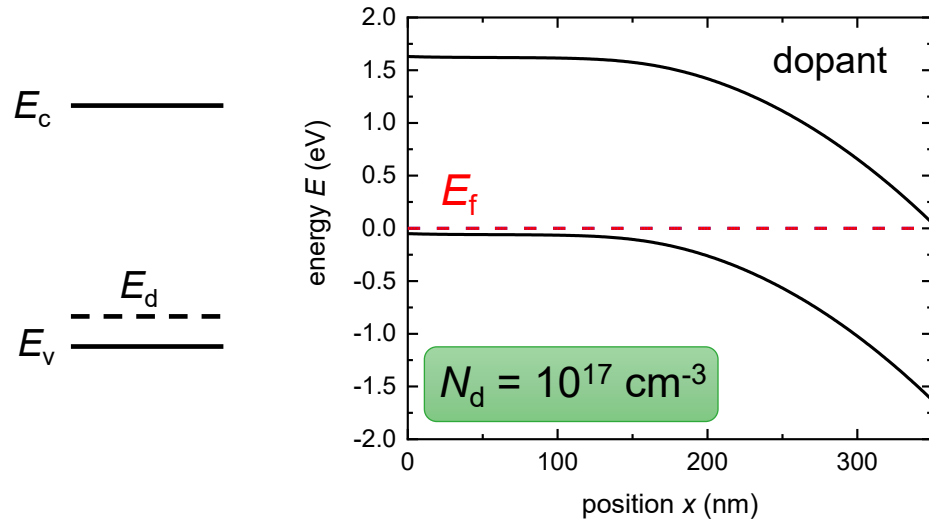
do dopants and defects have the same effect?



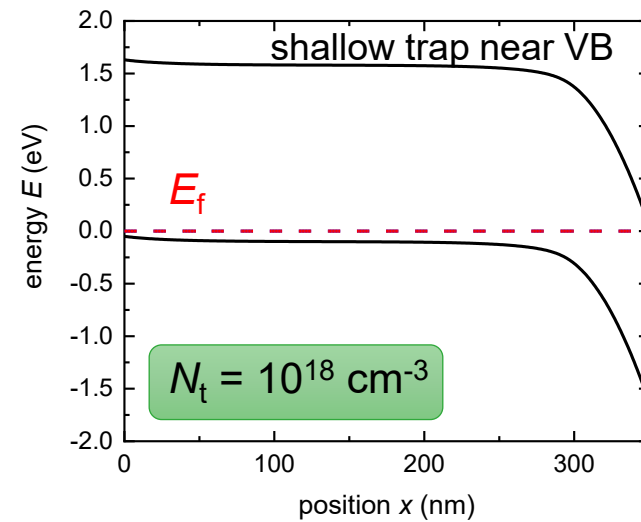
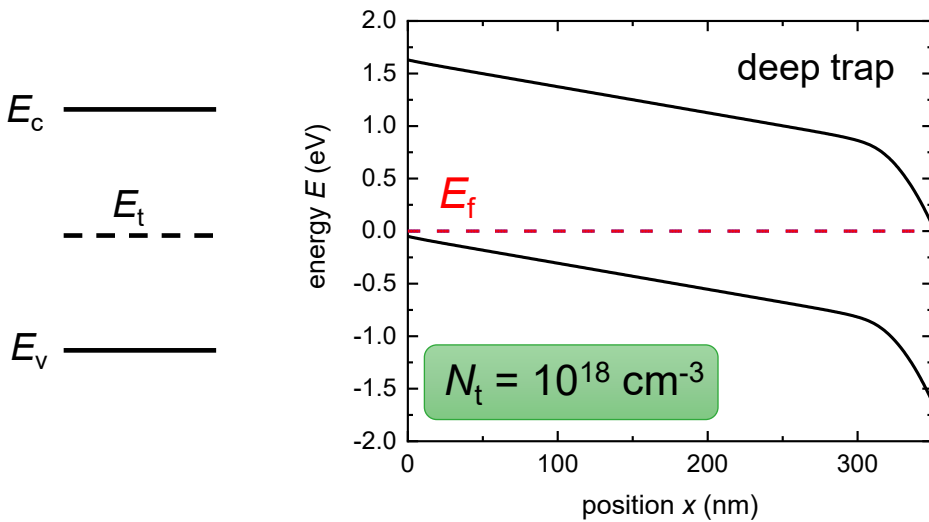
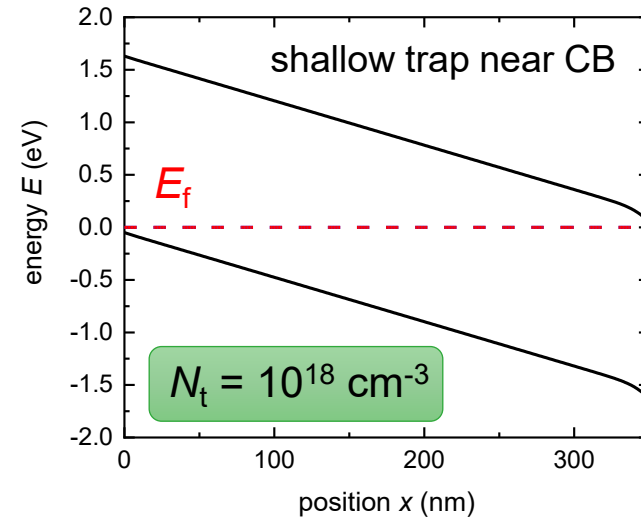
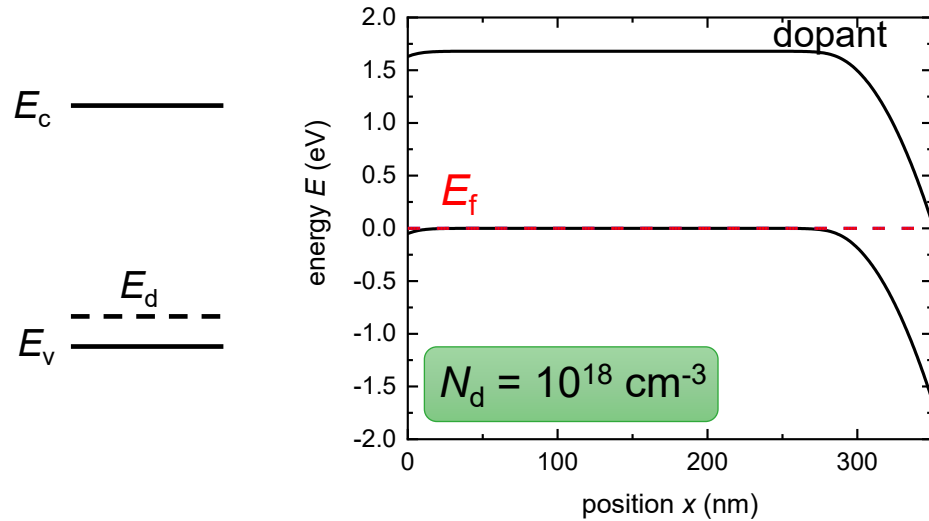
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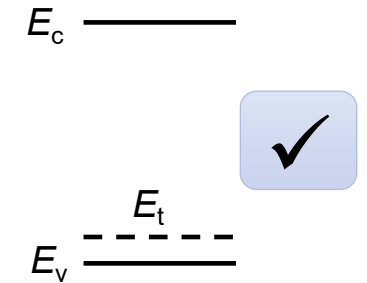
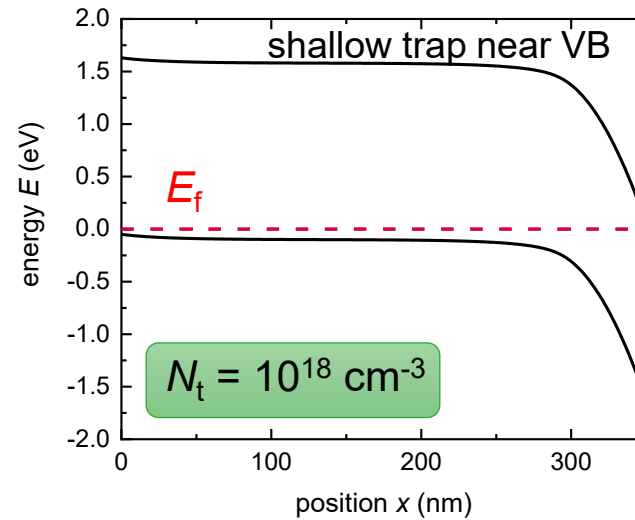
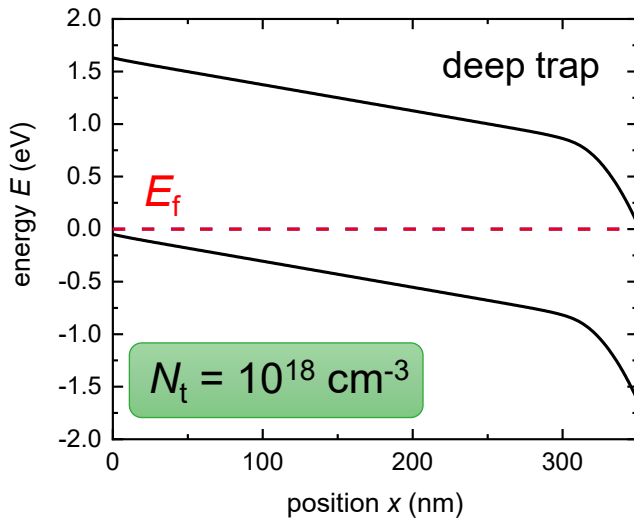
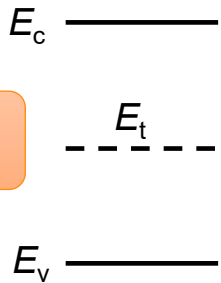
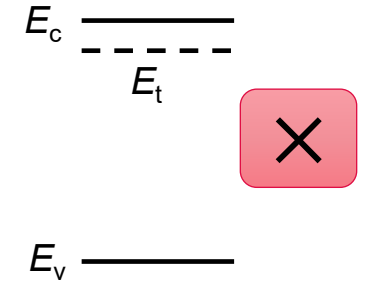
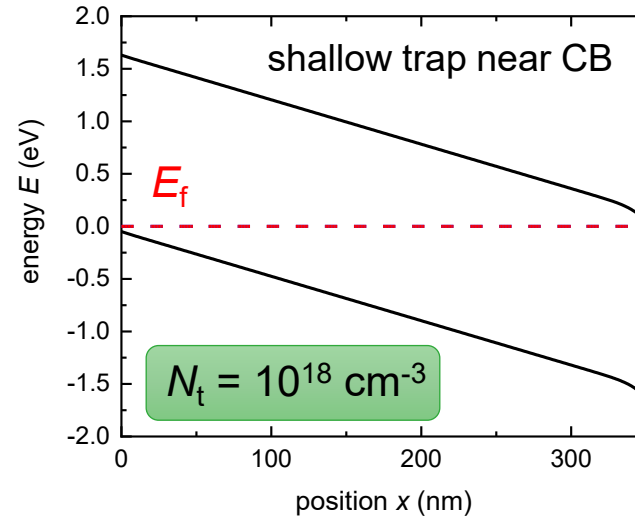
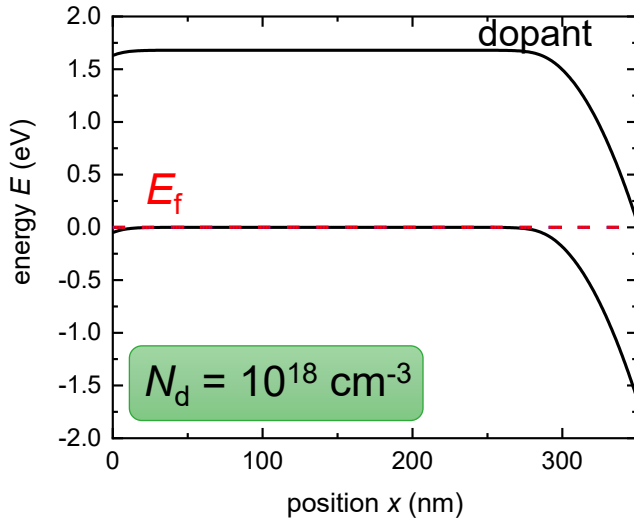
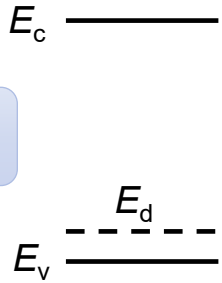
do dopants and defects have the same effect?



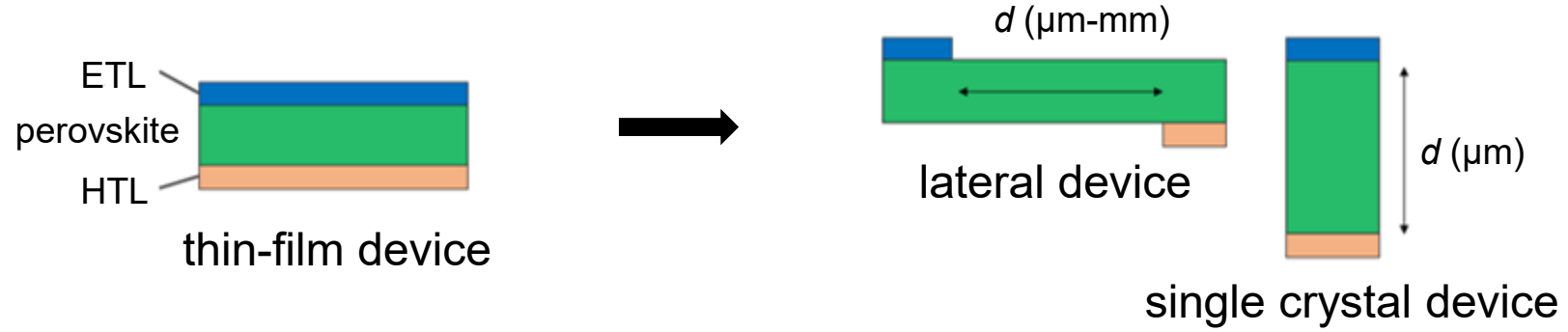
do dopants and defects have the same effect?



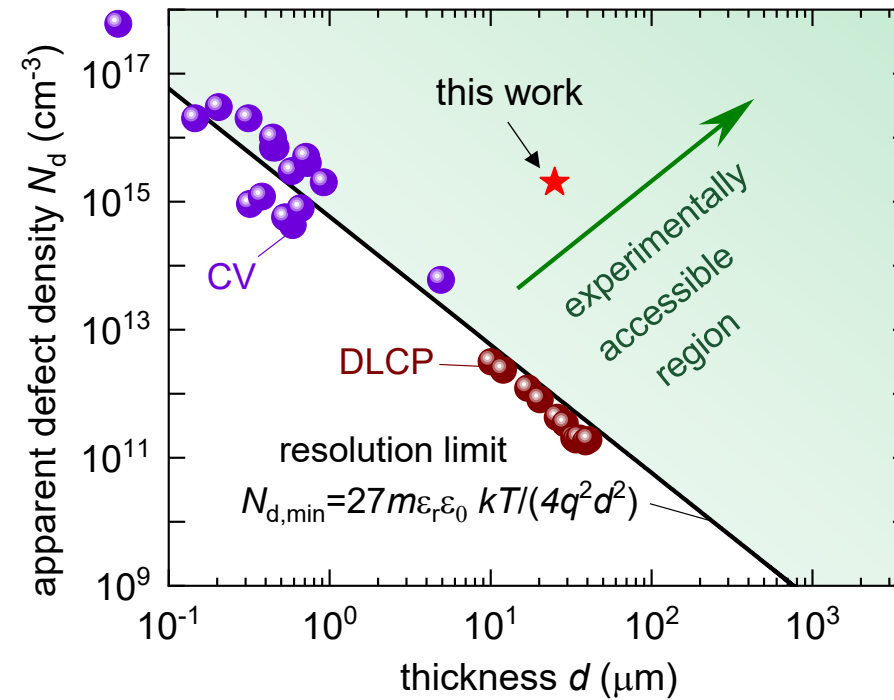
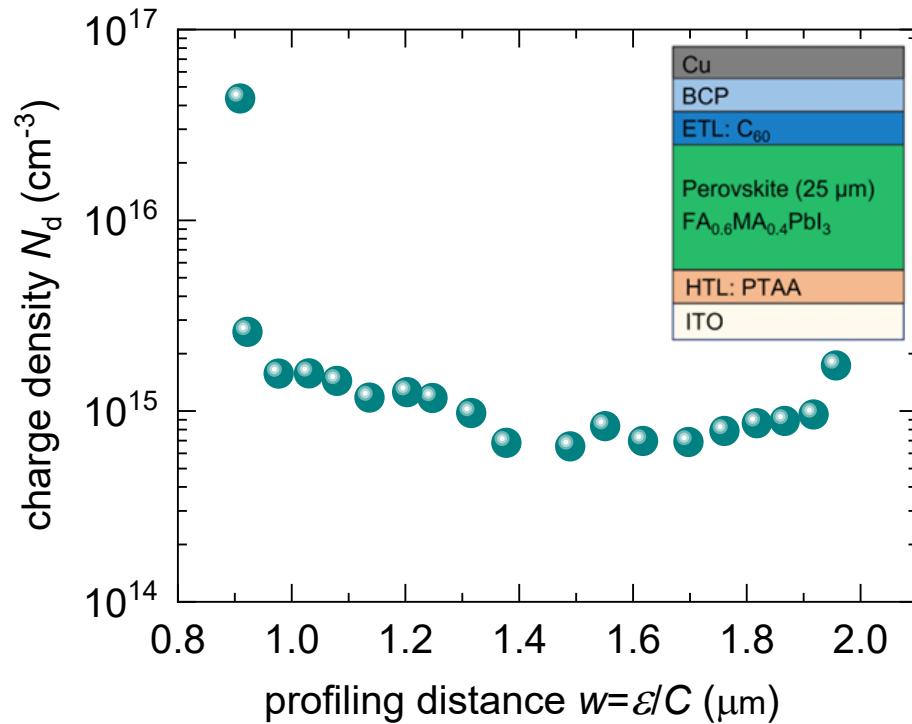
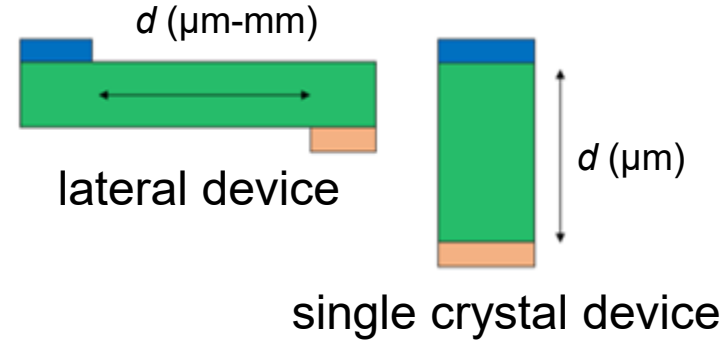
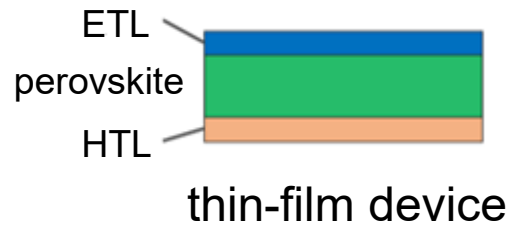
do dopants and defects have the same effect?



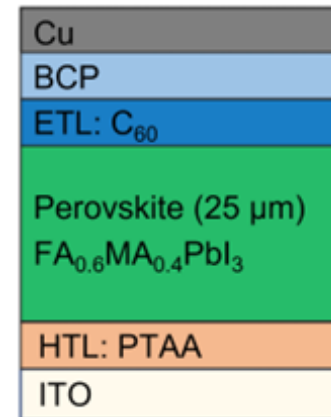
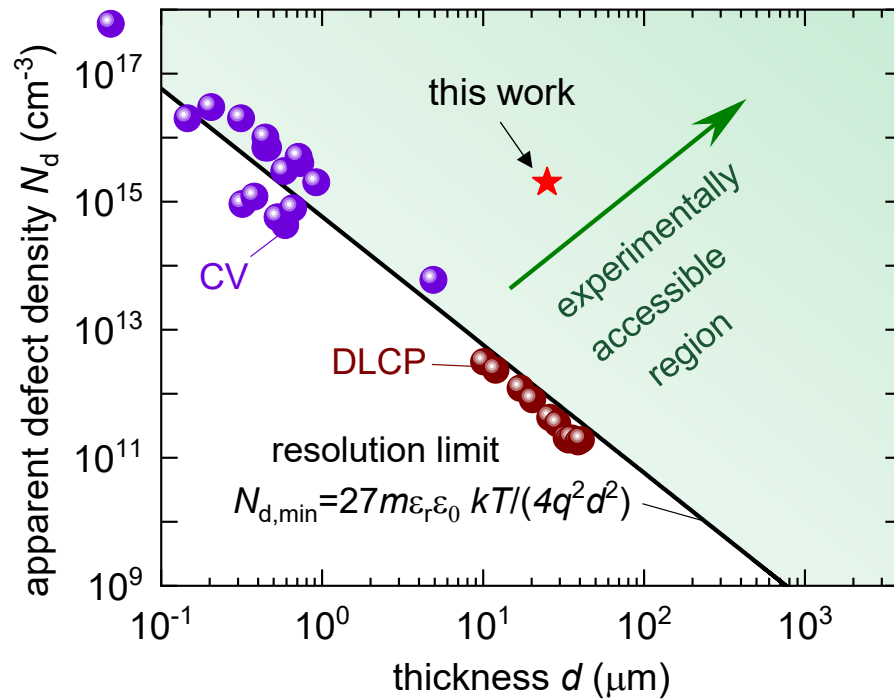
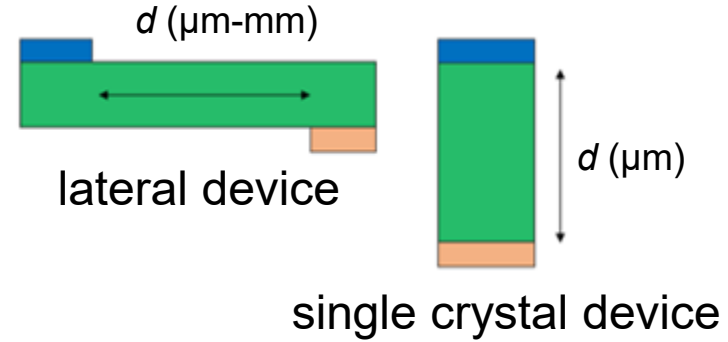
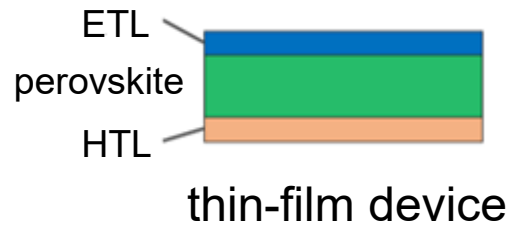
how to overcome the resolution limit?



how to overcome the resolution limit?

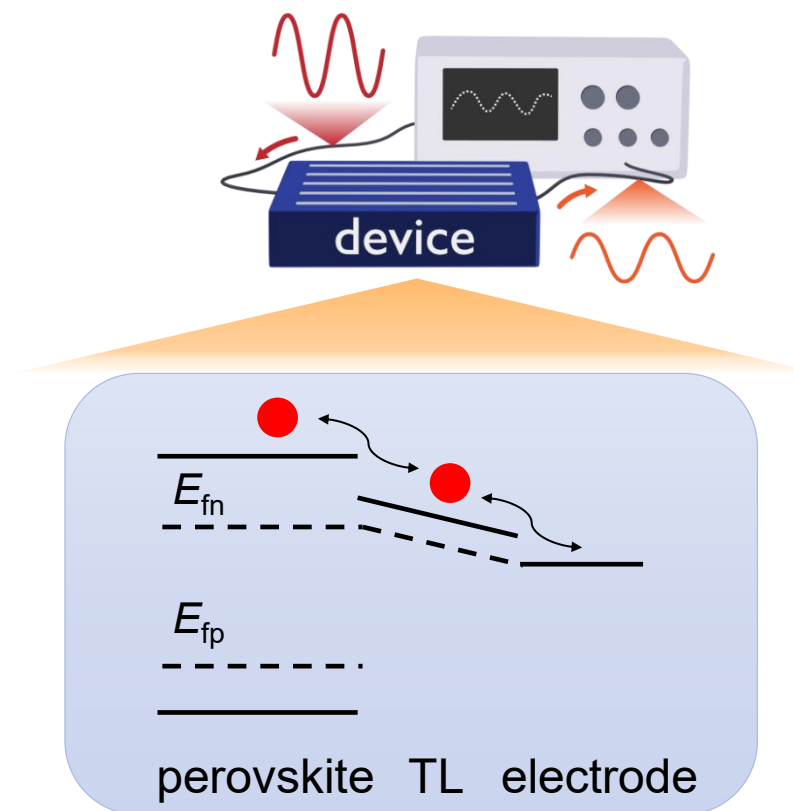


how to overcome the resolution limit?

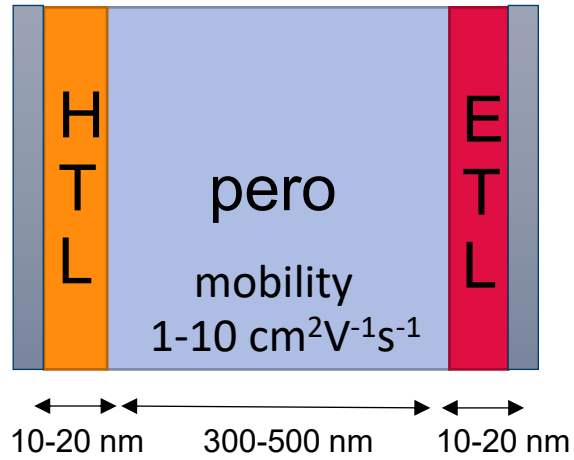


dopant-like shallow defects in single-crystal devices

characterizing charge extraction losses using small-perturbation methods



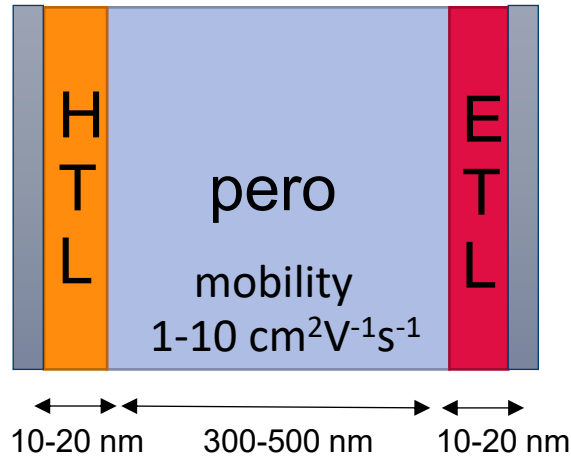
perovskite solar cell - effect of transport layers



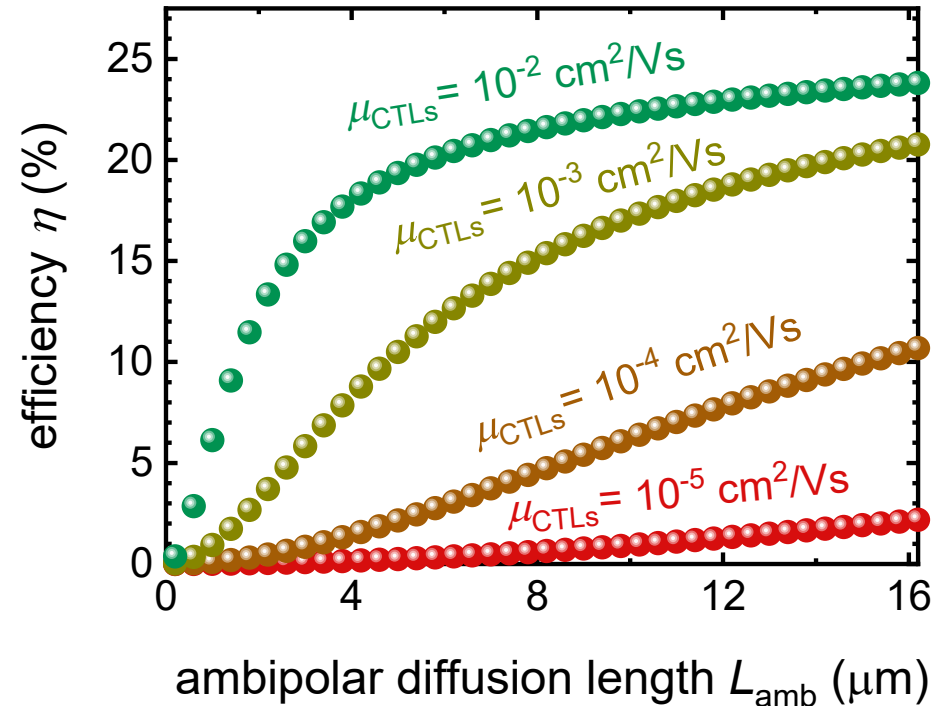
PTAA PCBM/BCP
P3HT C₆₀/BCP
SAMs CMC/BCP

mobility – $10^{-5}-10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

perovskite solar cell - effect of transport layers

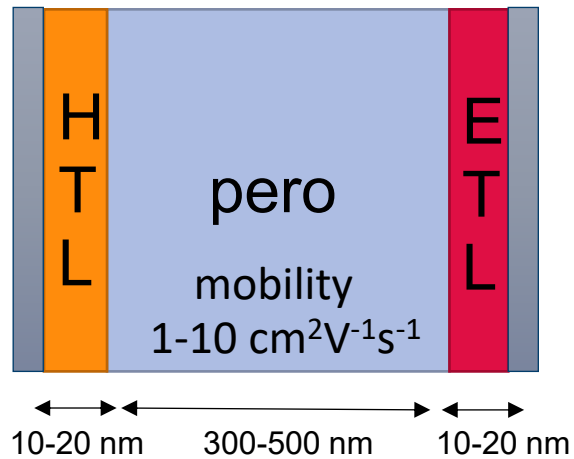


| | |
|---|----------------------|
| PTAA | PCBM/BCP |
| P3HT | C ₆₀ /BCP |
| SAMs | CMC/BCP |
| mobility – 10 ⁻⁵ -10 ⁻² cm ² V ⁻¹ s ⁻¹ | |

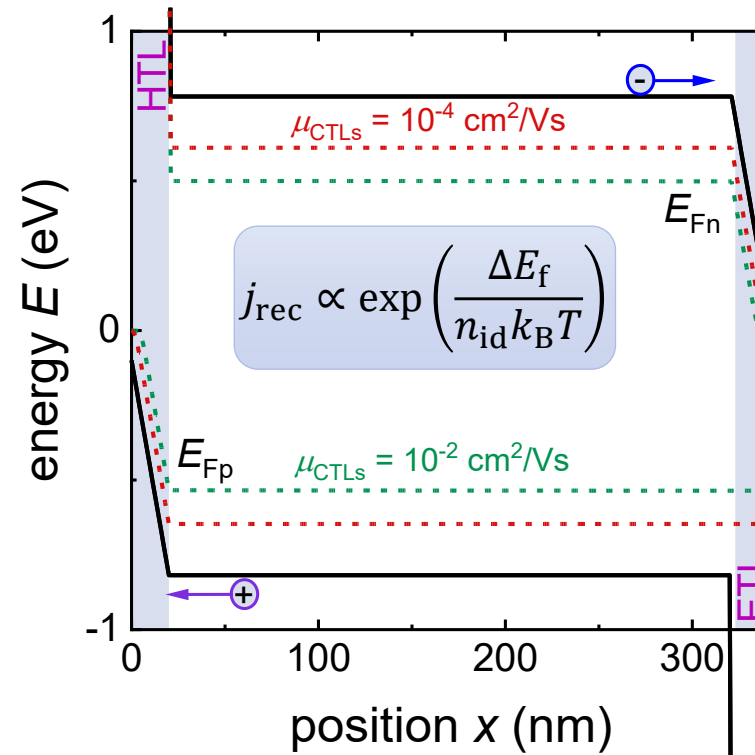


large diffusion lengths in the perovskite are irrelevant if transport layers do not extract charge efficiently

perovskite solar cell - effect of transport layers



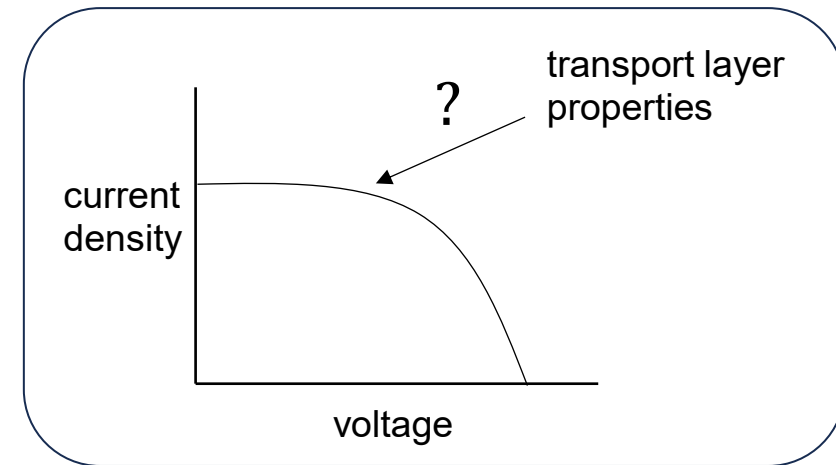
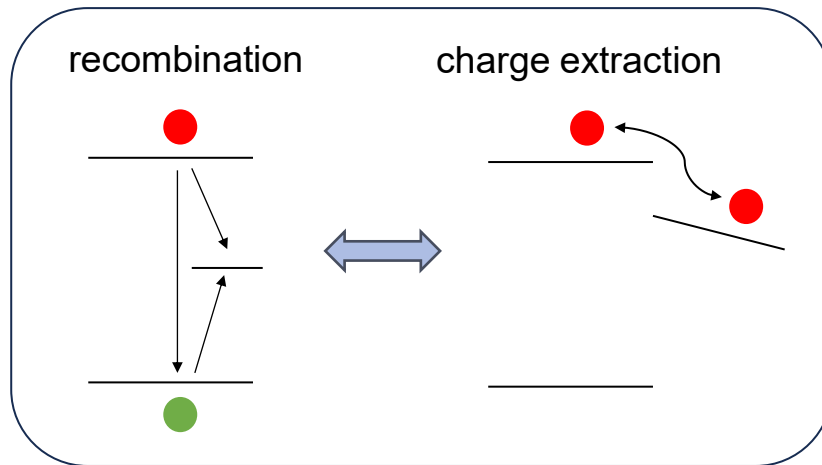
| | |
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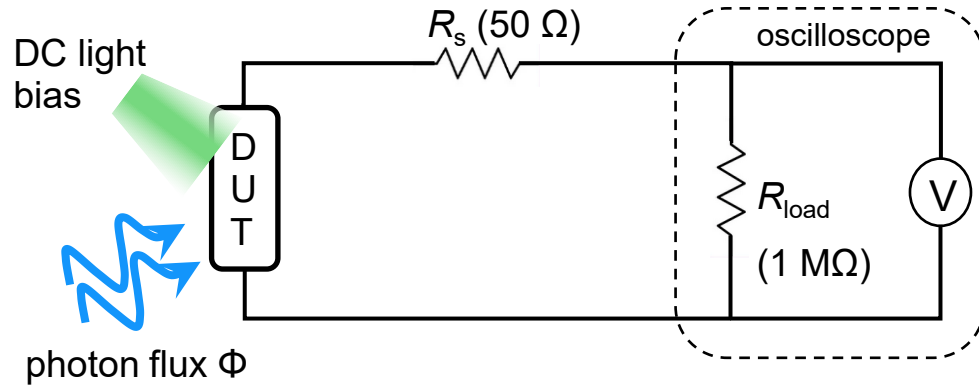
Fermi-level splitting in the perovskite is coupled to potential drop across the transport layers

can we separate transport layer effects from bulk effects in typical characterisation techniques?

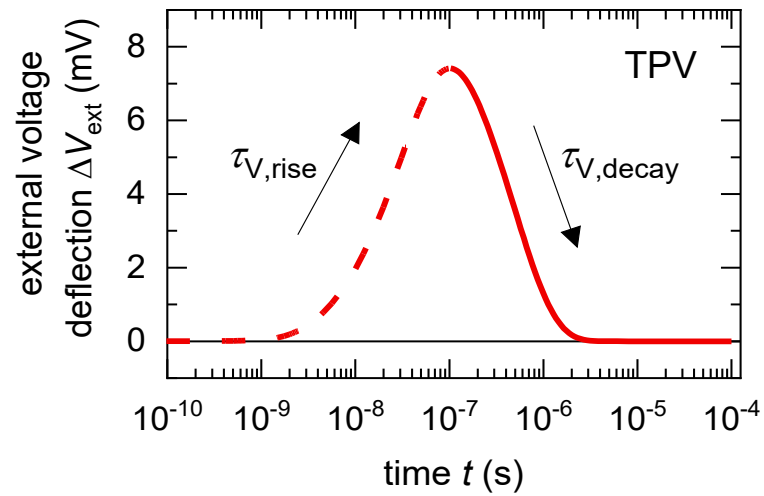
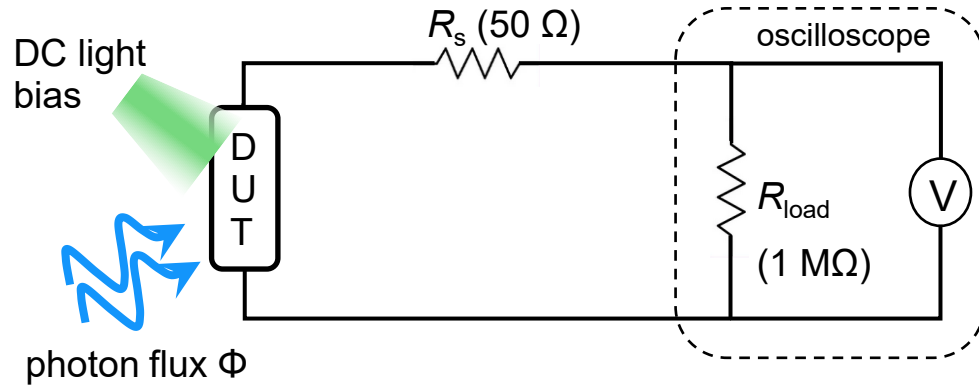
can we account for the effect of the transport layers on the PSC performance?



transient photovoltage (TPV) – time domain

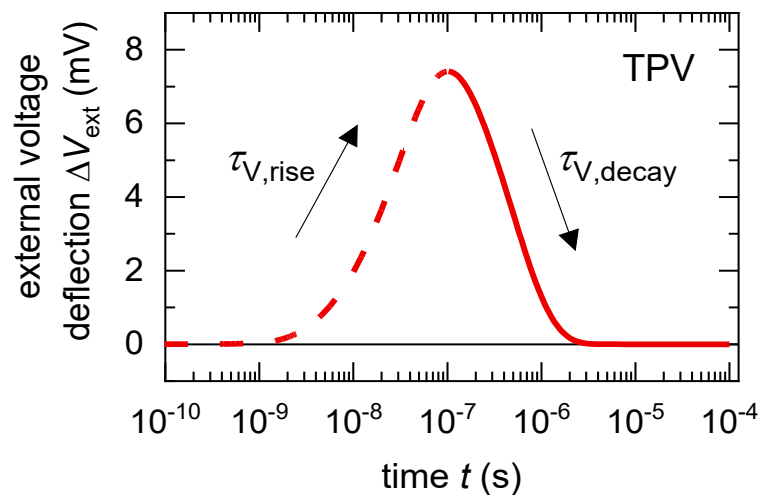
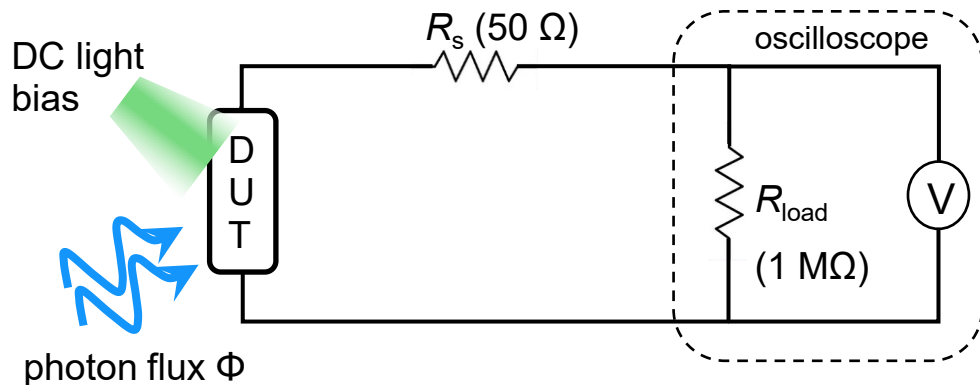


transient photovoltage (TPV) – time domain



$$\Delta V_{\text{ext}}(t) = \Delta V_{\text{ext},0} \left(e^{-t/\tau_{V,\text{decay}}} - e^{-t/\tau_{V,\text{rise}}} \right)$$

transient photovoltage (TPV) – time domain

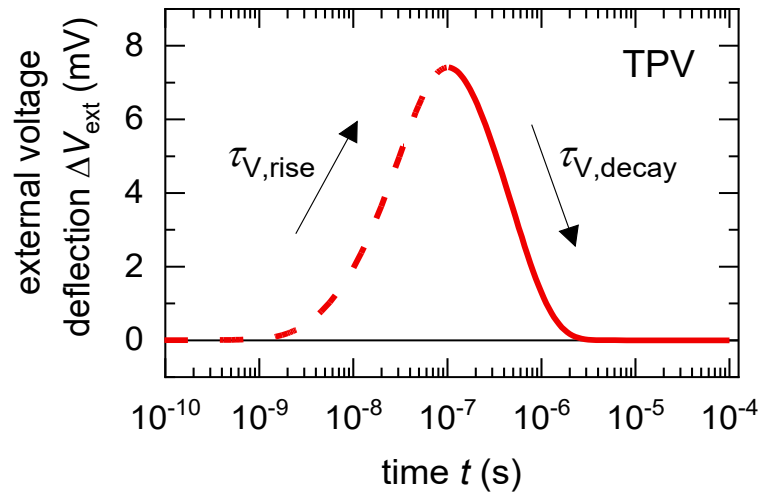
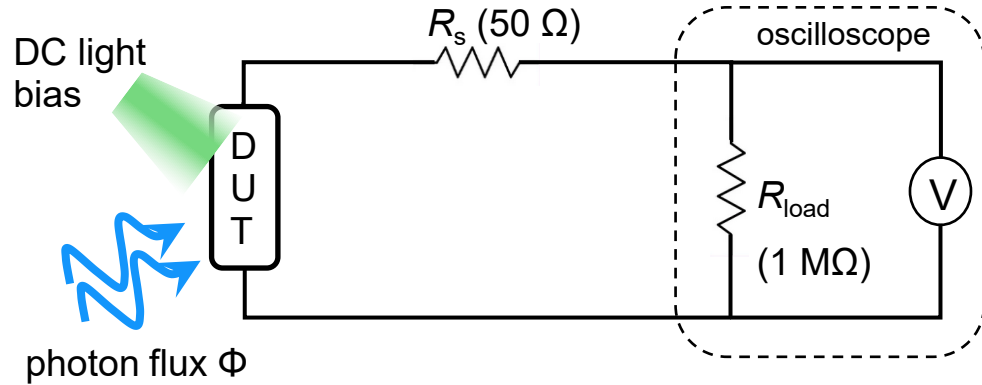


$$\Delta V_{\text{ext}}(t) = \Delta V_{\text{ext},0} \left(e^{-t/\tau_{V,\text{decay}}} - e^{-t/\tau_{V,\text{rise}}} \right)$$

intensity modulated photovoltage spectroscopy (IMVS) – frequency domain

$$W(\omega) = \frac{\tilde{V}}{q\tilde{\Phi}} \rightarrow \omega = 10 \text{ MHz} - 1 \text{ mHz}$$

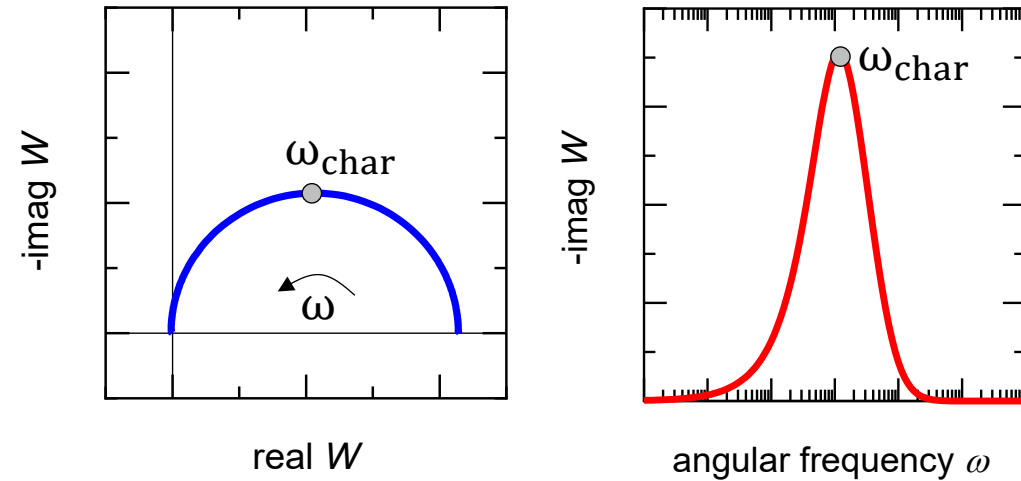
transient photovoltage (TPV) – time domain



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intensity modulated photovoltage spectroscopy (IMVS) – frequency domain

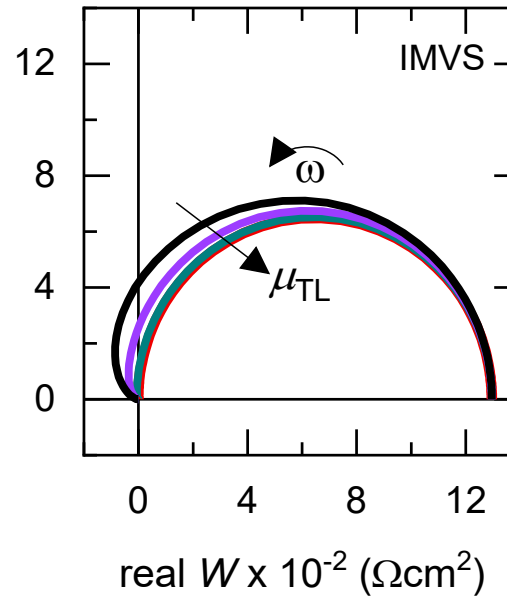
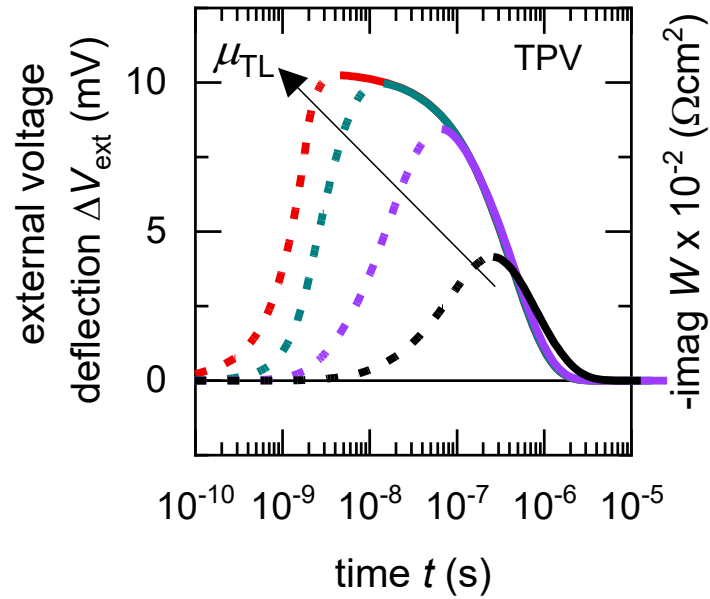
$$W(\omega) = \frac{\tilde{V}}{q\tilde{\Phi}} \rightarrow \omega = 10 \text{ MHz} - 1 \text{ mHz}$$



$$\frac{d(-\text{imag } W)}{d\omega} = 0 \rightarrow \omega_{\text{char}} = \frac{1}{\tau_{\text{char}}}$$

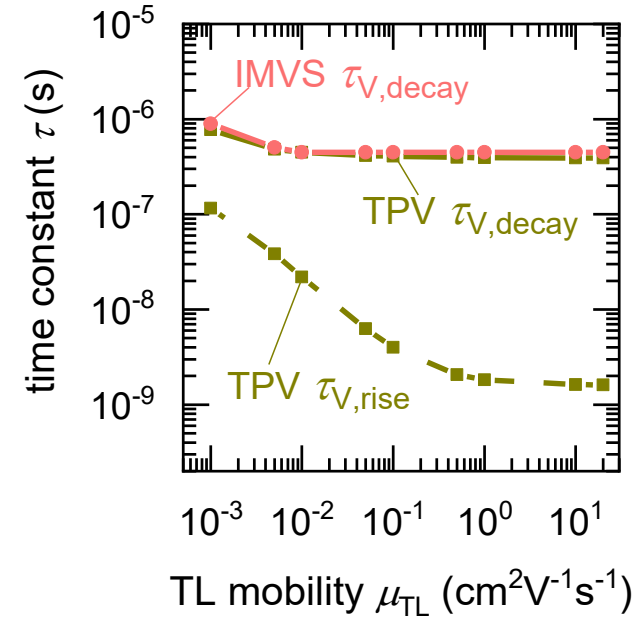
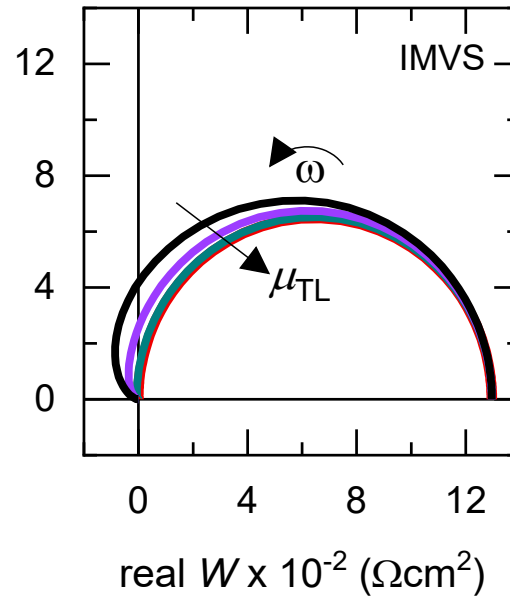
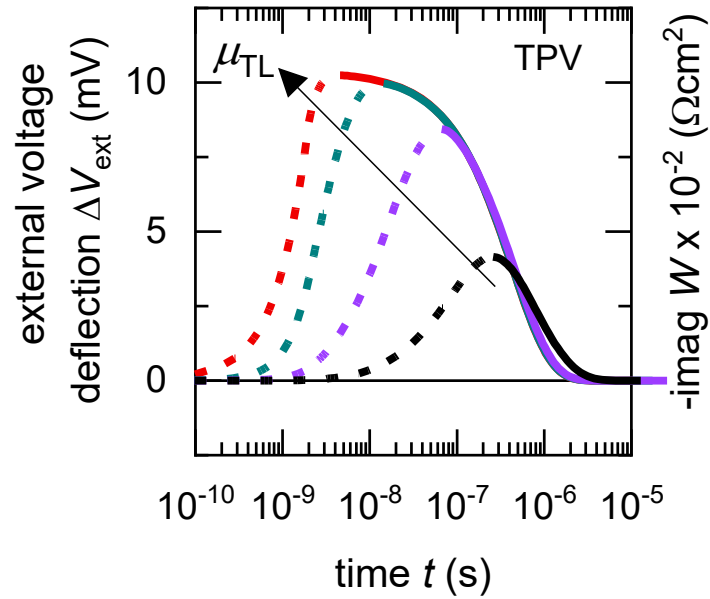
time constants

drift-diffusion simulations

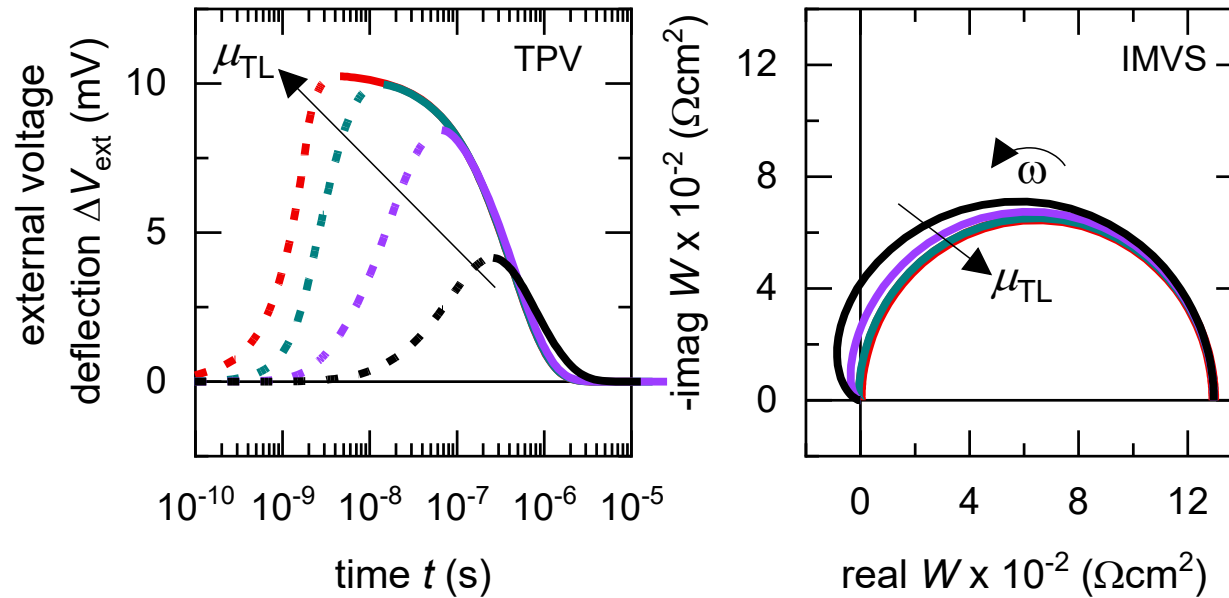


time constants

drift-diffusion simulations



why do time domain methods show two time constants while frequency domain methods show only one time constant?

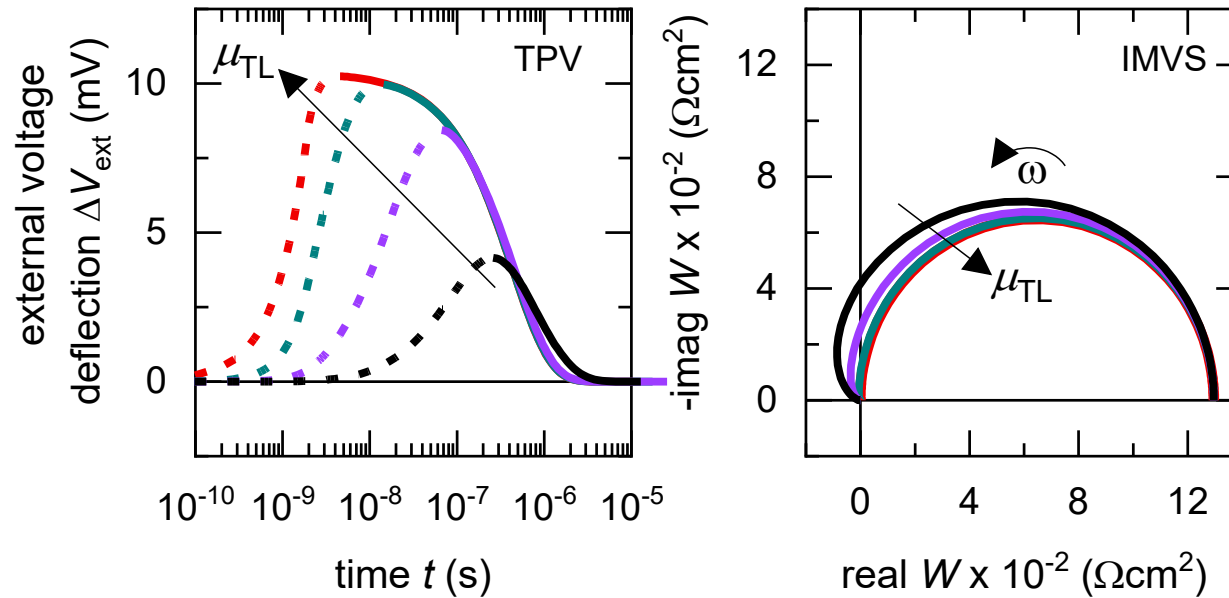


logic

time domain methods show absolute value and slope of the voltage/current

frequency domain methods show no information about the slope

$$V \rightarrow \frac{dV}{dt} \xrightarrow{\text{laplace transform}} i\omega V$$



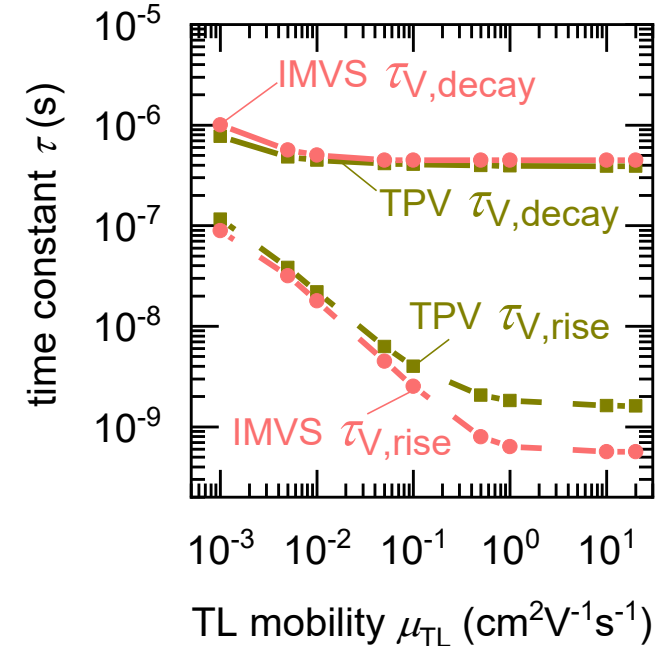
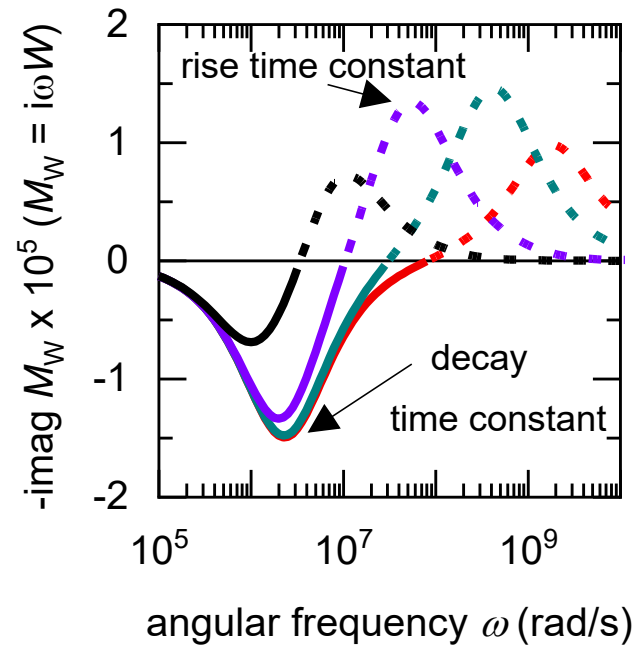
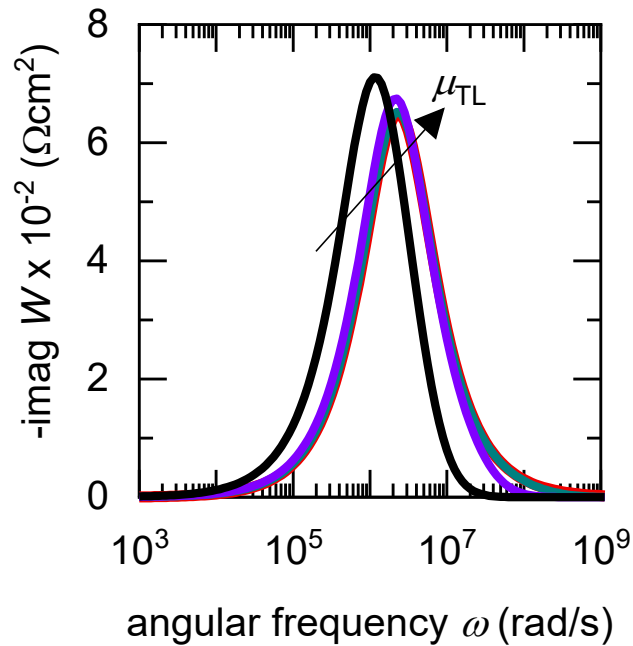
logic

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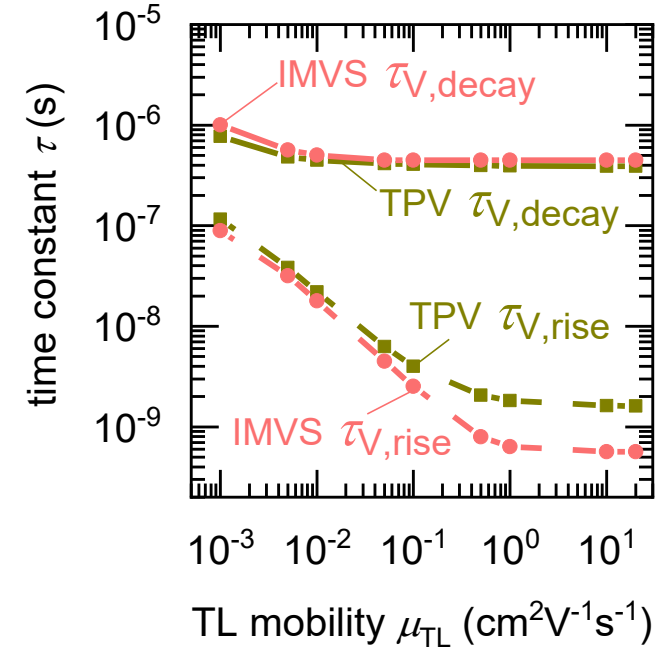
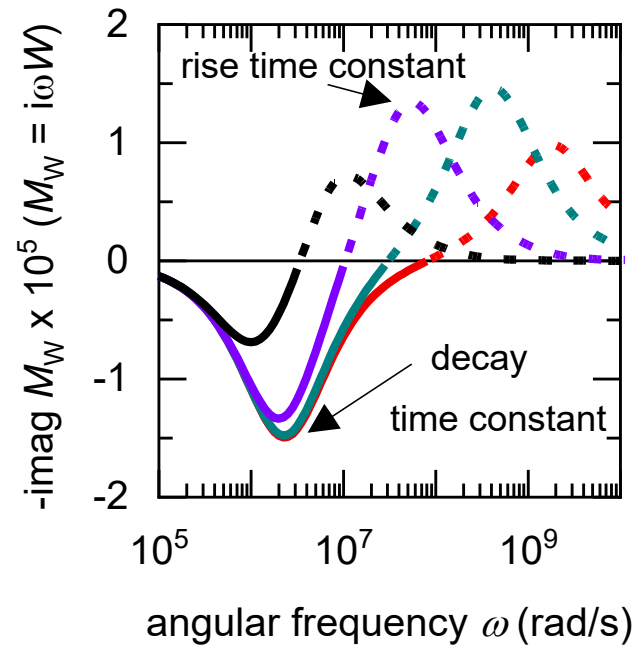
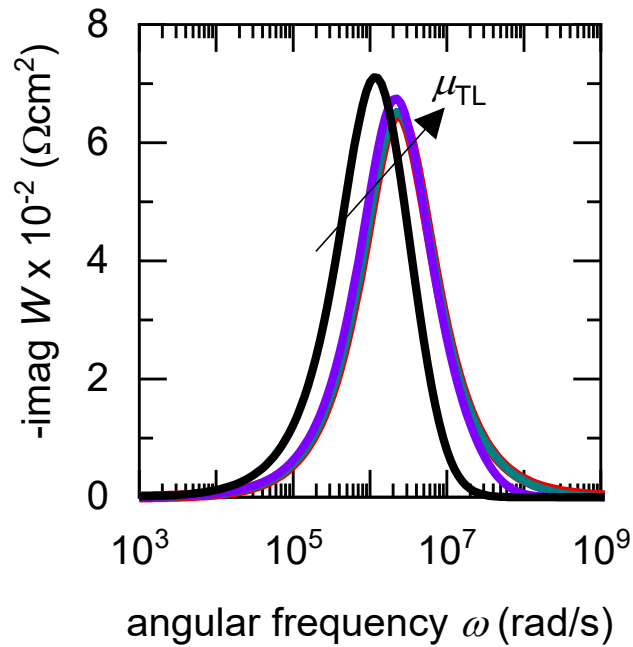
$$M_W = i\omega W \longrightarrow \begin{matrix} \text{real } M_W = -\omega \times \text{imag } W \\ \text{imag } M_W = \omega \times \text{real } W \end{matrix} \longrightarrow \frac{d(-\text{imag } M_W)}{d\omega} = 0 \rightarrow \omega_{\text{char}} = \frac{1}{\tau_{\text{char}}}$$

modified transfer function



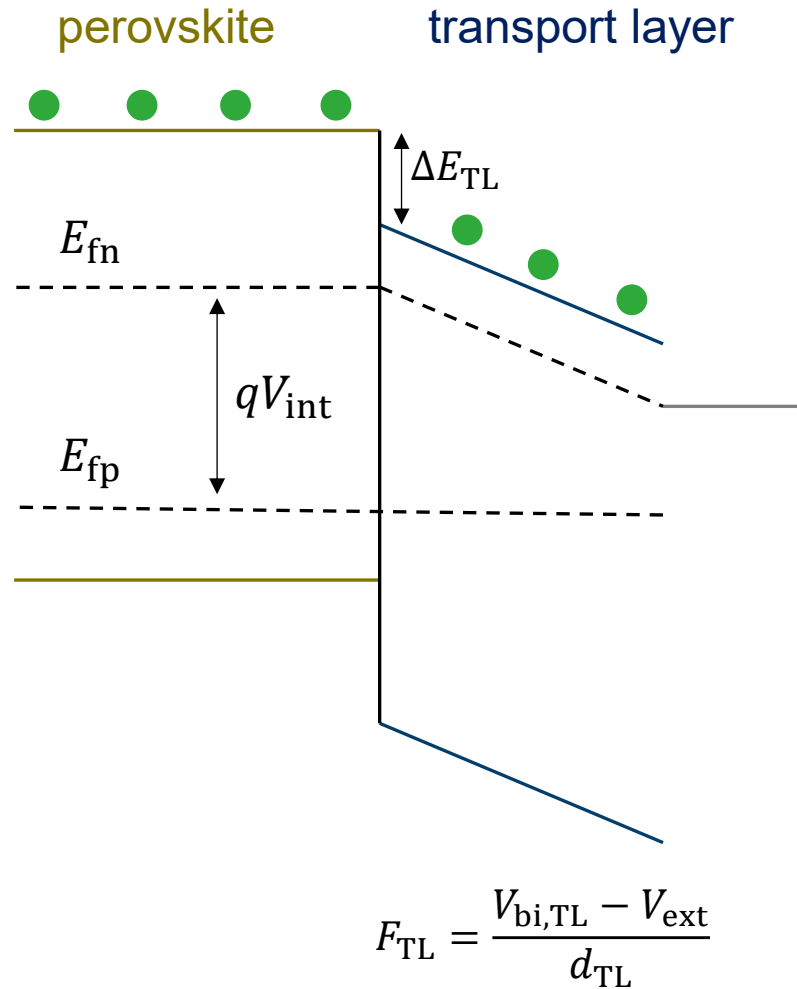
rise time constant embedded in the transition of real part of IMVS transfer function to negative values at high frequencies

modified transfer function



which mechanisms generate the rise and decay time constants?

charge extraction through the transport layer



current density

$$j = qn_i S_{exc} \times \left[\exp\left(\frac{qV_{int}}{2k_B T}\right) - \exp\left(\frac{V_{ext}}{2k_B T}\right) \right]$$

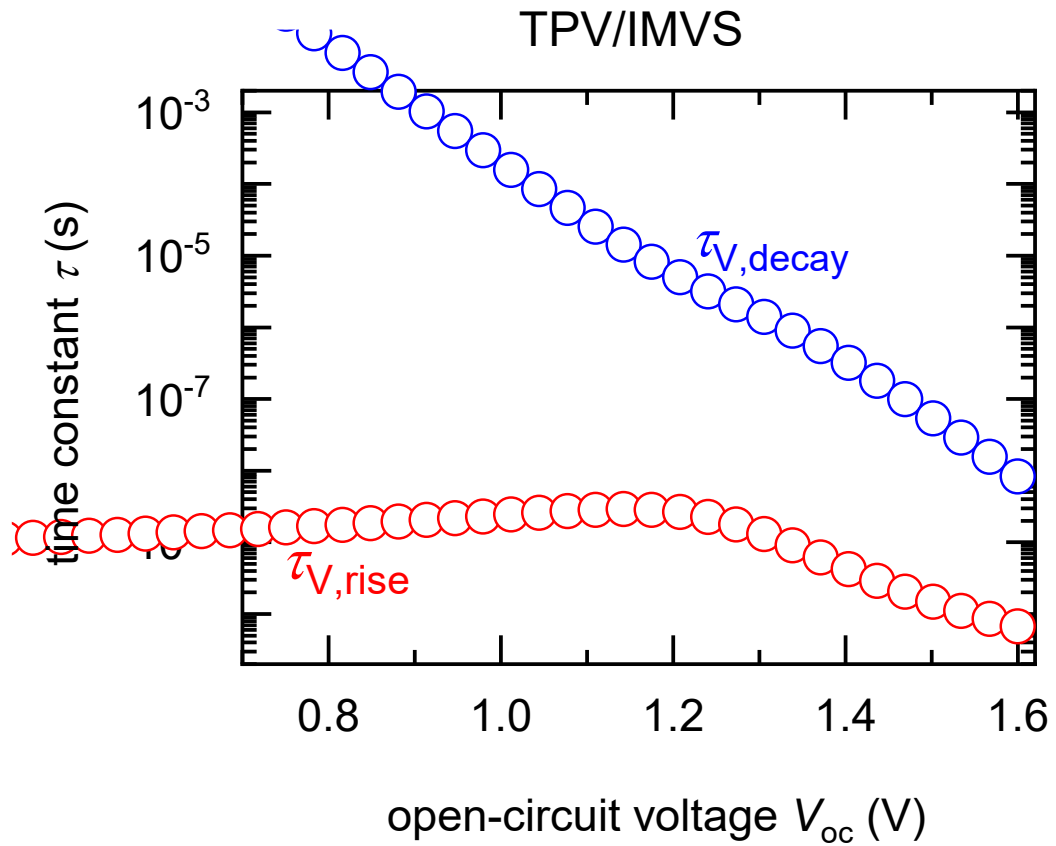
charge extraction velocity

$$S_{exc}(V_{elec}) \cong \mu_{TL} F_{TL} \exp\left(\frac{\Delta E_{TL}}{k_B T}\right)$$

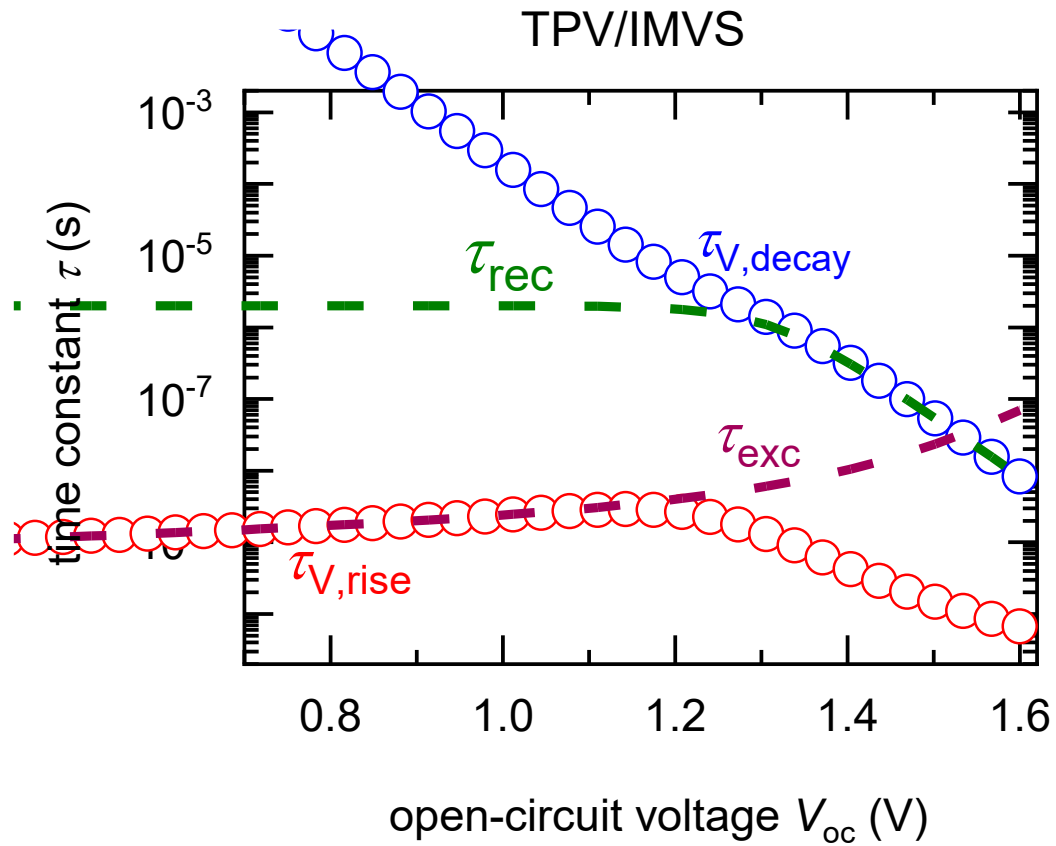
charge extraction time constant

$$\tau_{exc} = \frac{d_{pero}}{S_{exc}}$$

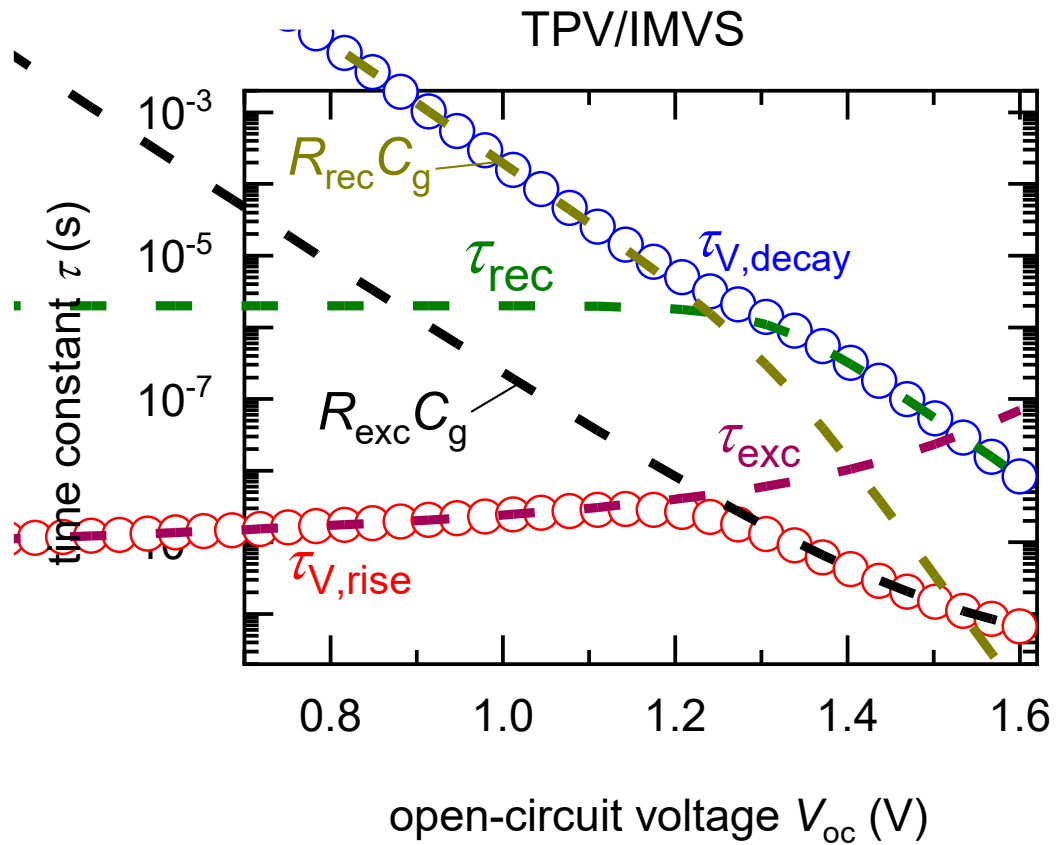
predicted time constants



predicted time constants

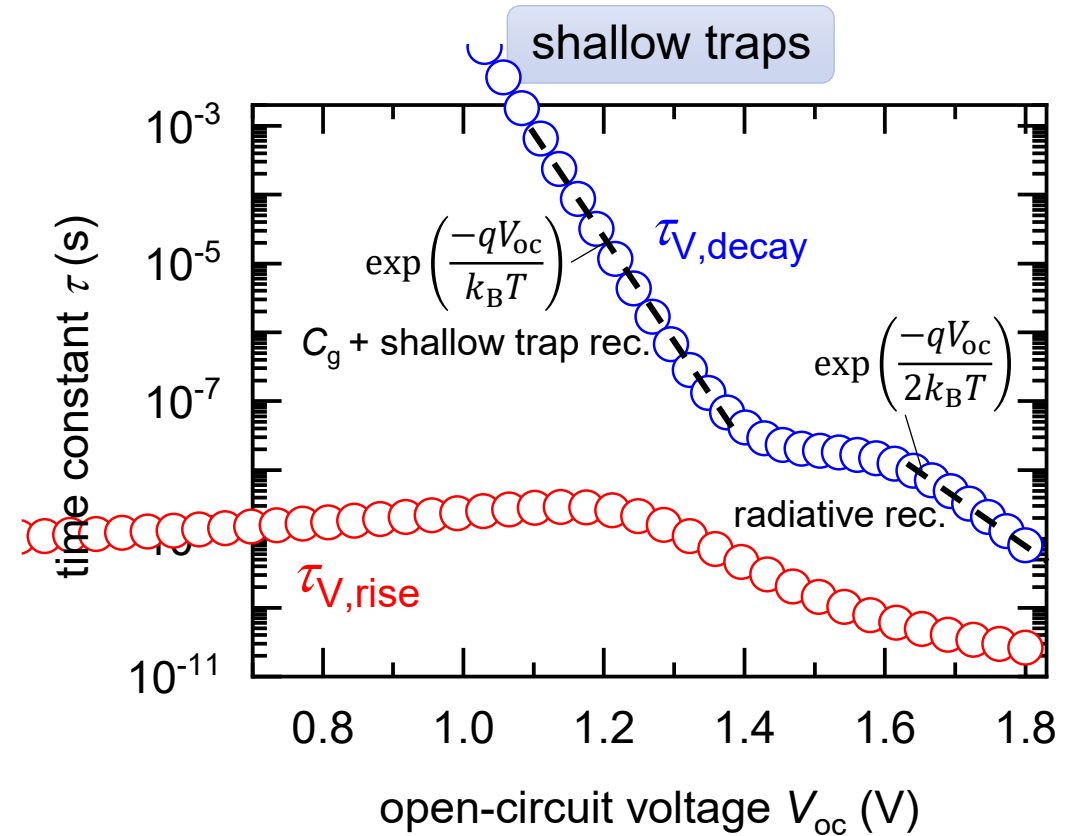
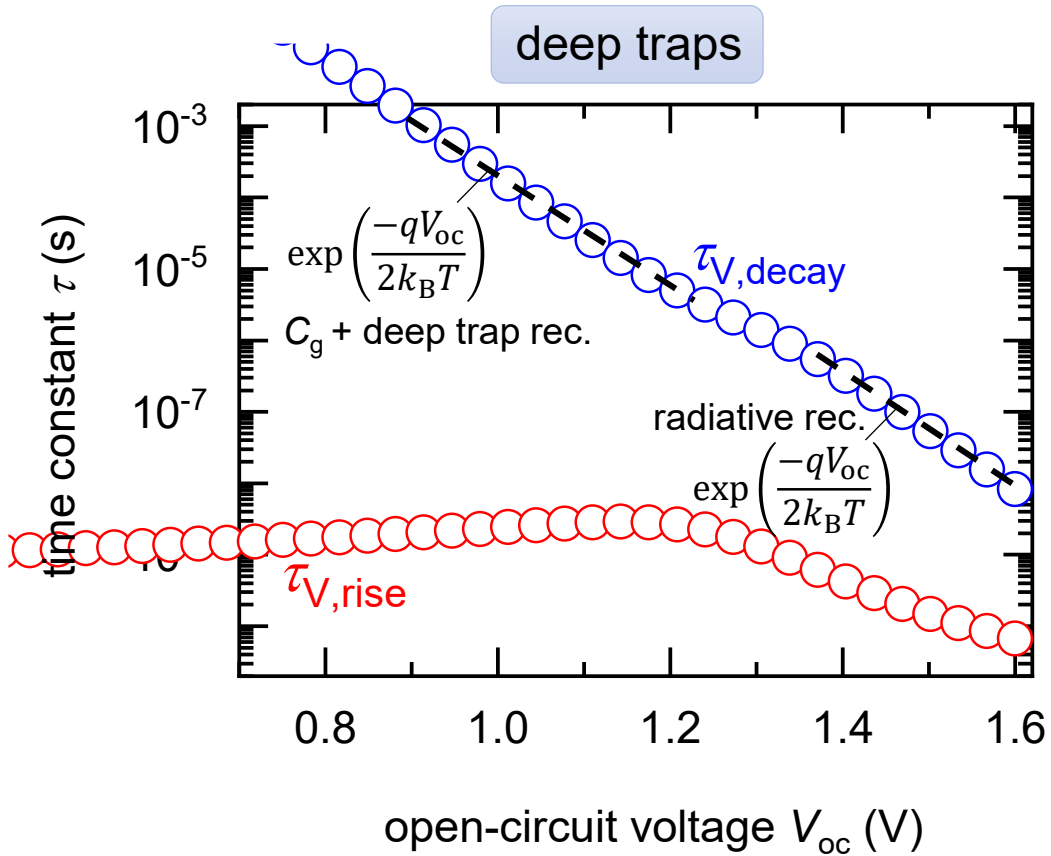


predicted time constants



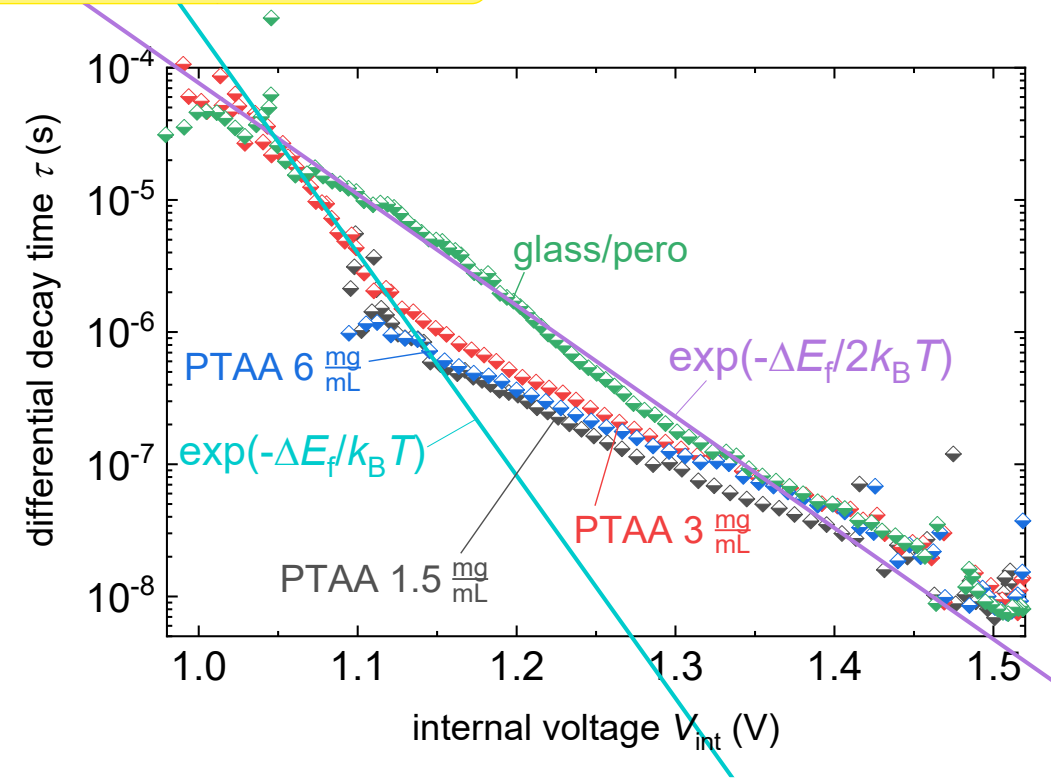
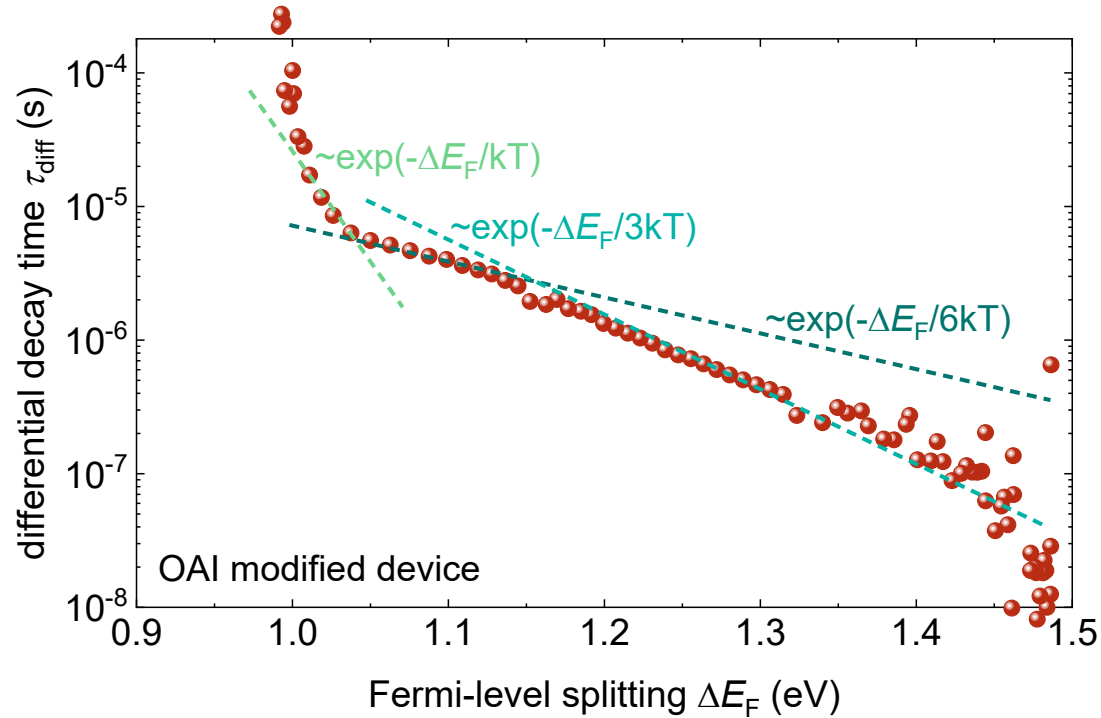
rise time constants mostly correspond to charge extraction
decay time constants correspond to recombination

predicted time constants



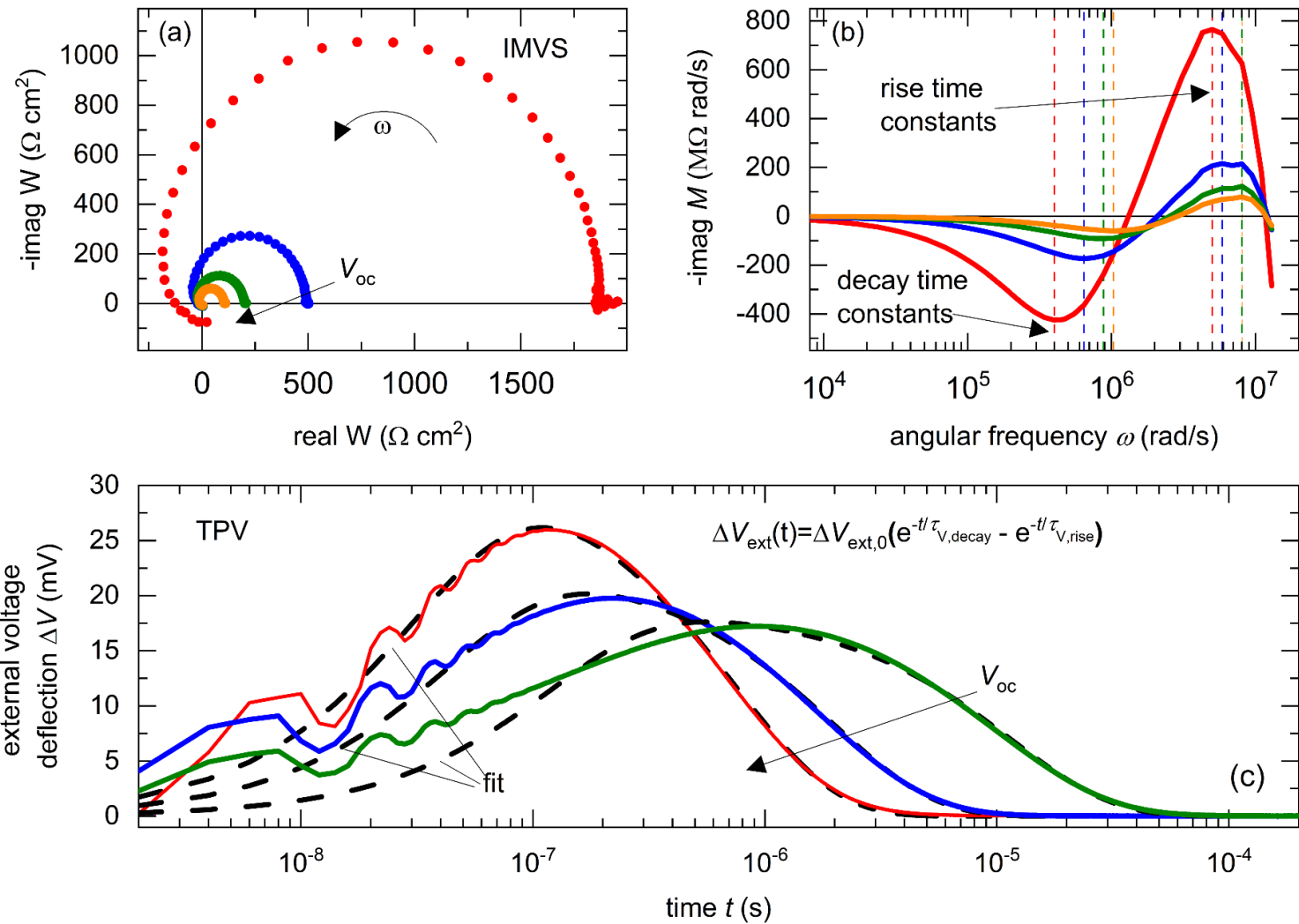
shallow traps in perovskite solar cells

transient photoluminescence (tr-PL) measurements

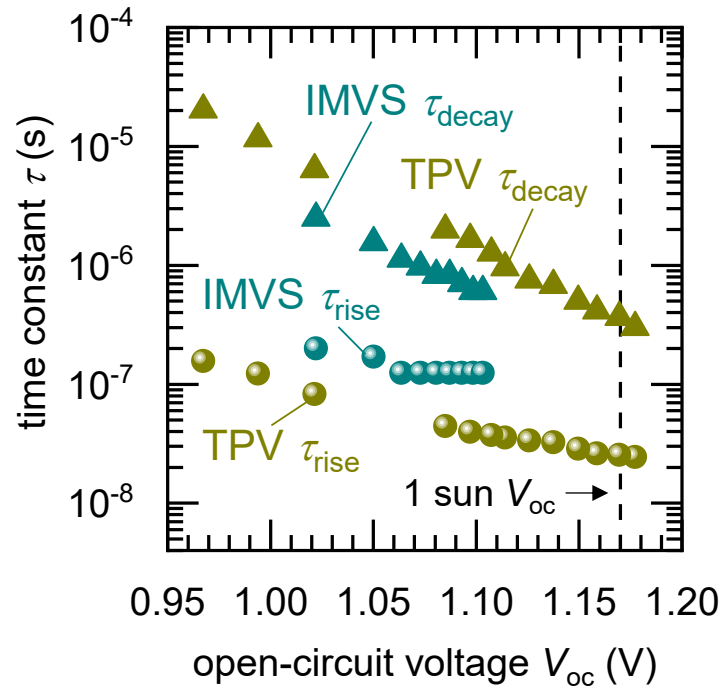


application to experimental data

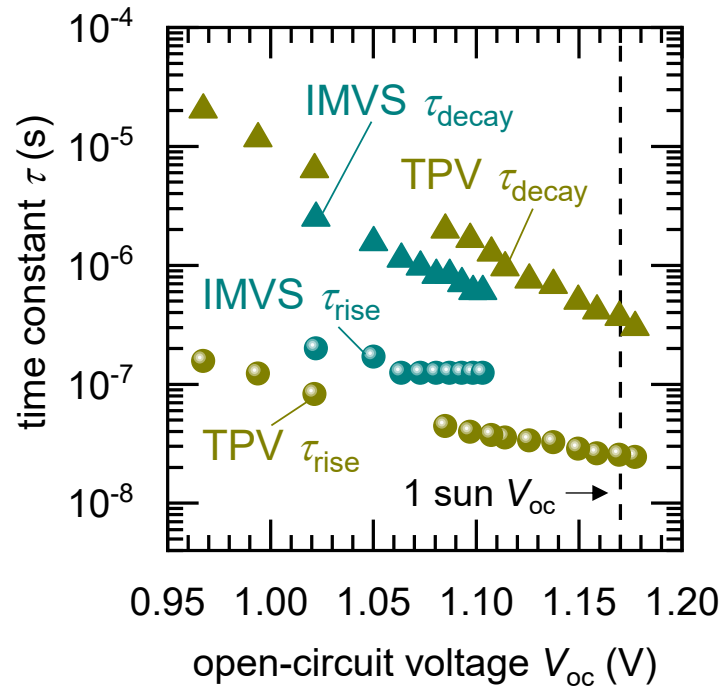
ITO/SAMs/PTAA/Cs_{0.05}FA_{0.8}MA_{0.15}PbI_{2.25}Br_{0.75} (1.68 eV)/C₆₀/BCP/Ag devices



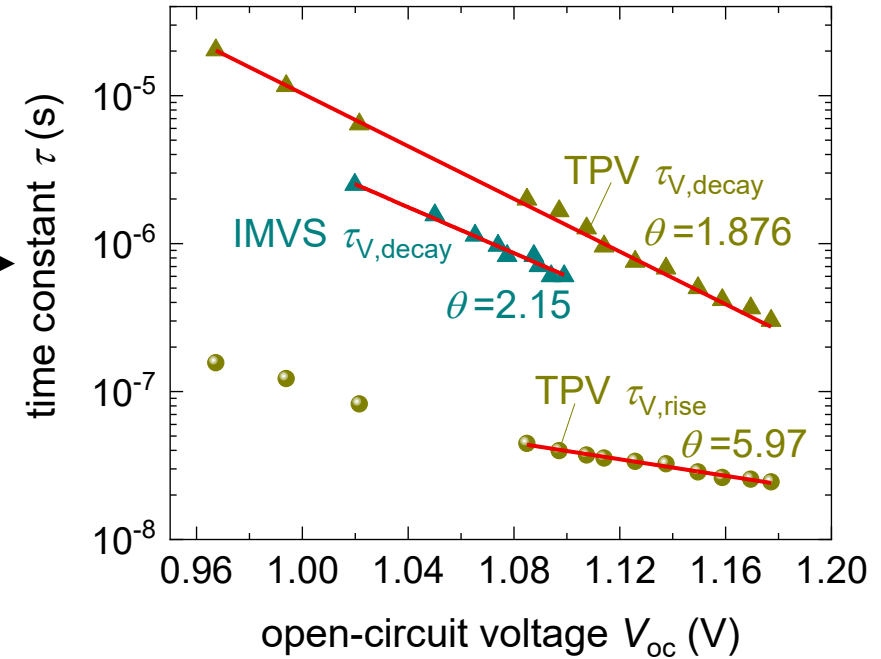
experimental rise and decay time constants



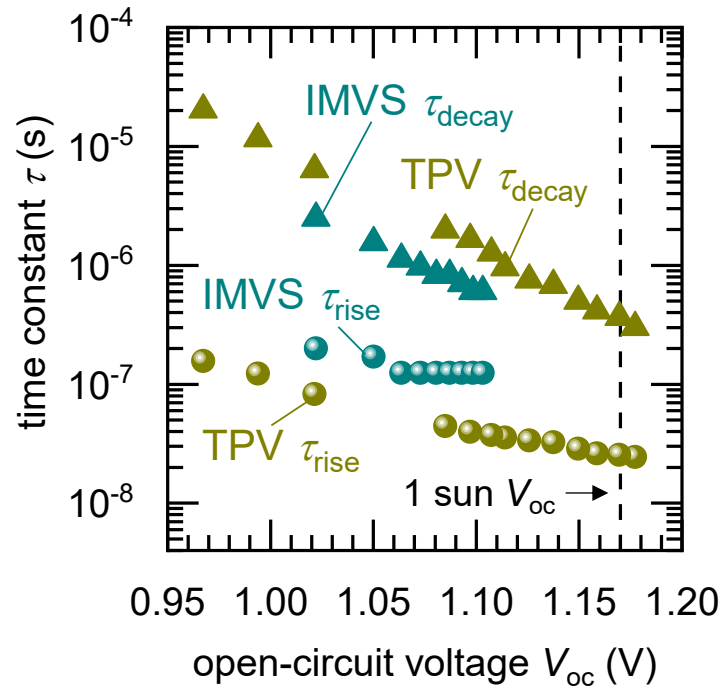
experimental rise and decay time constants



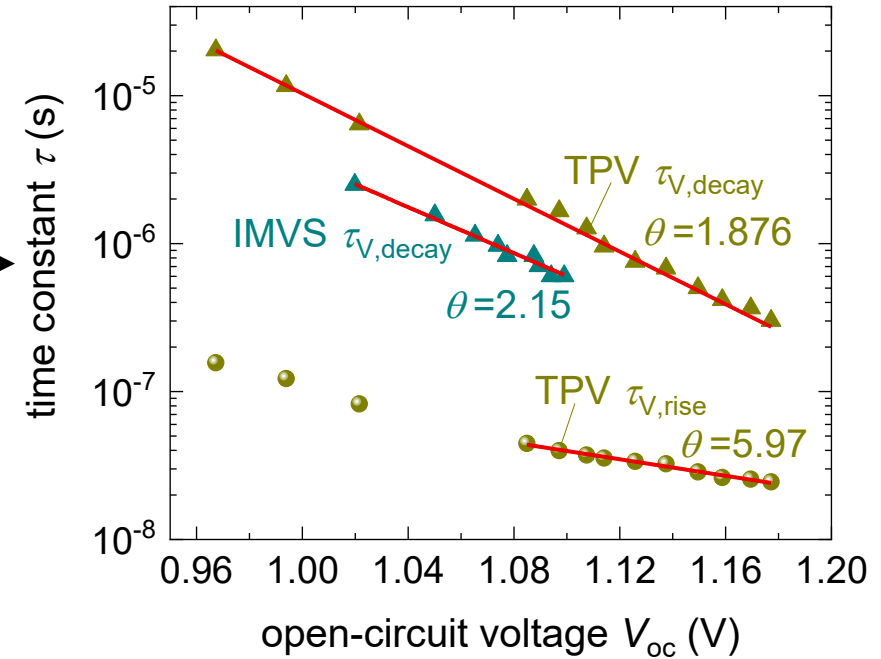
$$\tau = \tau_0 \exp\left(\frac{-qV_{oc}}{\theta k_B T}\right)$$



experimental rise and decay time constants



$$\tau = \tau_0 \exp\left(\frac{-qV_{oc}}{\theta k_B T}\right)$$



rise times correspond to charge extraction

decay times correspond to recombination limited by charge re-injection from the electrodes

figure of merit accounting for charge extraction losses

$$j = qd \left(G - \frac{n_i}{\tau_{\text{rec}}} \left[\exp \left(\frac{qV_{\text{ext}}}{n_{\text{id}} k_B T} \right) - 1 \right] \right)$$

current-voltage curve – balance of generation and recombination

figure of merit accounting for charge extraction losses

$$j = \left[\frac{1}{1 + \frac{\tau_{\text{exc}}}{\tau_{\text{rec}}}} \right] qd \left(G - \frac{n_i}{\tau_{\text{rec}}} \left[\exp \left(\frac{qV_{\text{ext}}}{n_{\text{id}} k_B T} \right) - 1 \right] \right)$$

current-voltage curve including generation, recombination and extraction

figure of merit accounting for charge extraction losses

$$j = \left[\frac{1}{1 + \frac{\tau_{\text{exc}}}{\tau_{\text{rec}}}} \right] qd \left(G - \frac{n_i}{\tau_{\text{rec}}} \left[\exp \left(\frac{qV_{\text{ext}}}{n_{\text{id}}k_{\text{B}}T} \right) - 1 \right] \right)$$

$$\text{FOM} = \frac{1}{1 + \frac{\tau_{\text{exc}}}{\tau_{\text{rec}}}}$$

FOM = 1
perfect charge extraction

FOM < 1
non-ideal charge extraction

figure of merit accounting for charge extraction losses

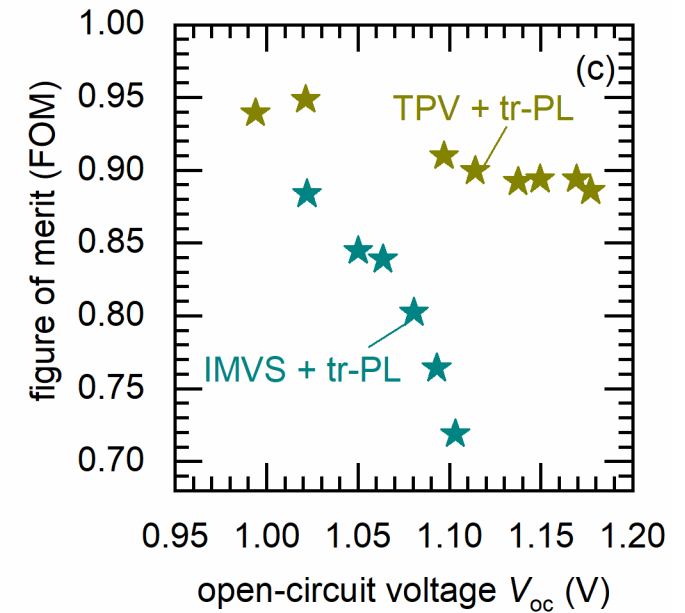
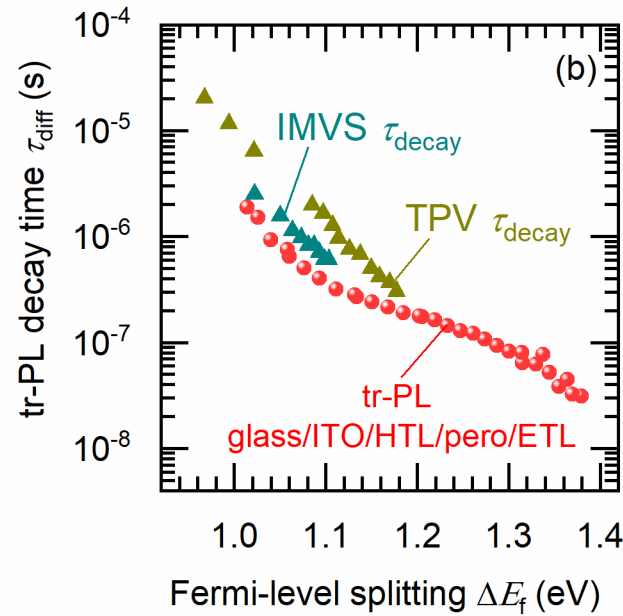
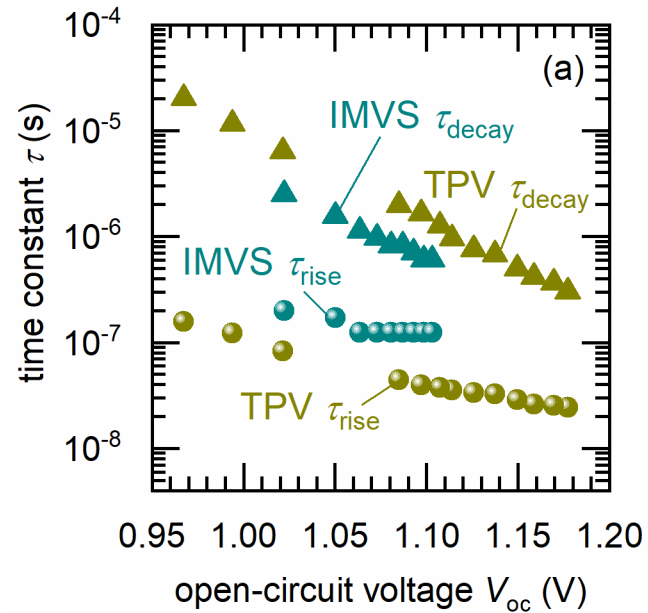
$$j = \left[\frac{1}{1 + \frac{\tau_{\text{exc}}}{\tau_{\text{rec}}}} \right] qd \left(G - \frac{n_i}{\tau_{\text{rec}}} \left[\exp \left(\frac{qV_{\text{ext}}}{n_{\text{id}} k_B T} \right) - 1 \right] \right)$$

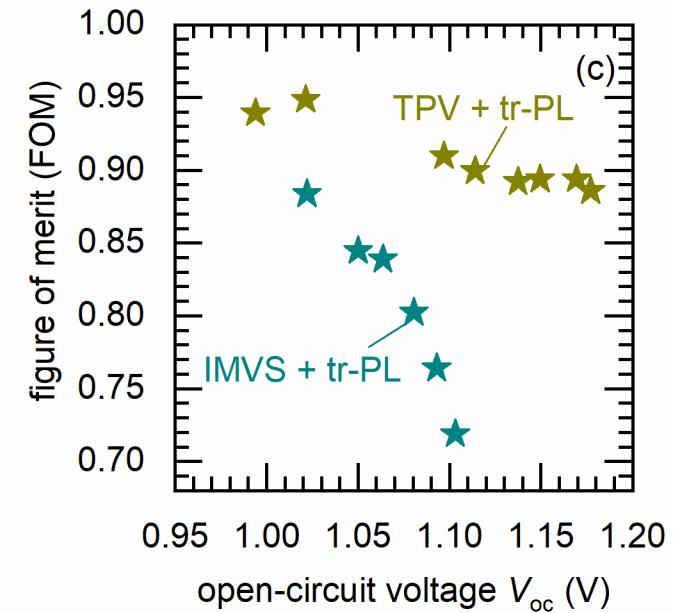
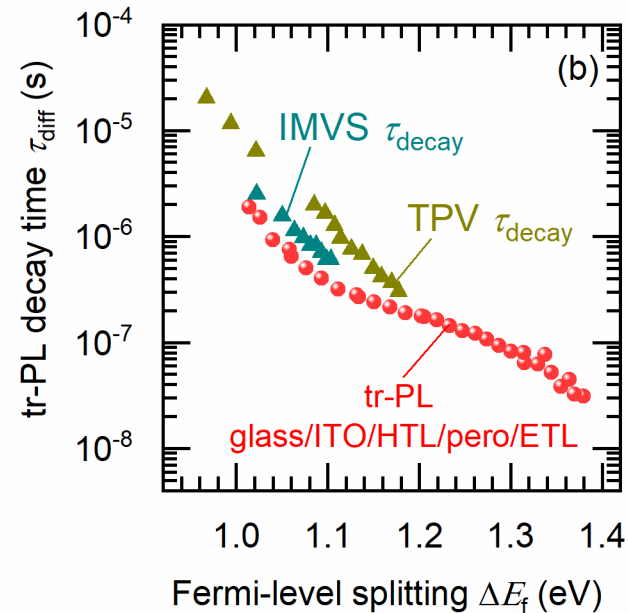
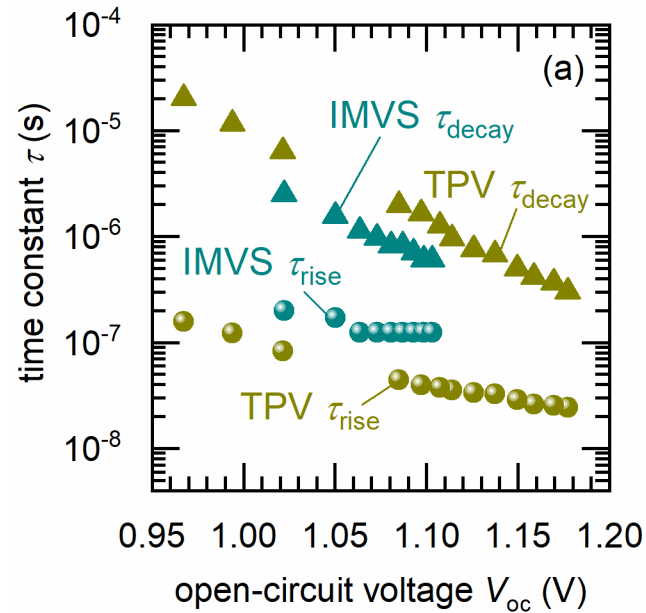


$$\text{FOM} = \frac{1}{1 + \frac{\tau_{\text{exc}}}{\tau_{\text{rec}}}}$$

$$\tau_{\text{exc}} = \tau_{\text{rise}} \quad \tau_{\text{rec}} = ?$$

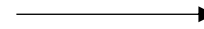
how to determine the recombination lifetime?





FOM values close to 1 imply a significant electric field in the transport layers that allows fast charge extraction

Can we resolve doping and defect densities from overlapping mechanisms in capacitance measurements?

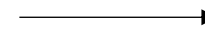


resolution limit

$$N_{d,\min} = \frac{27m_{CV}k_B T \epsilon_r \epsilon_0}{4q^2 d^2}$$

conclusions

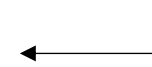
Can we resolve doping and defect densities from overlapping mechanisms in capacitance measurements?



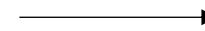
resolution limit

$$N_{d,\min} = \frac{27m_{CV}k_B T \epsilon_r \epsilon_0}{4q^2 d^2}$$

thin-film PSCs have low deep-defect densities but significant shallow defect densities



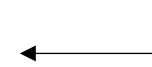
Can we resolve doping and defect densities from overlapping mechanisms in capacitance measurements?



resolution limit

$$N_{d,\min} = \frac{27m_{CV}k_B T \epsilon_r \epsilon_0}{4q^2 d^2}$$

thin-film PSCs have low deep-defect densities but significant shallow defect densities



can we separate transport layer effects from bulk effects in typical characterization techniques?

$i\omega \times$ transfer function
verify using time-domain methods

rise time constant \rightarrow charge extraction
decay time constant \rightarrow recombination

can we account for the effect of the transport layers on the PSC performance?



charge extraction efficiency

$$FOM(V) = \frac{1}{1 + \frac{\tau_{exc}(V)}{\tau_{rec}(V)}}$$

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Cite this: *Energy Environ. Sci.*,
2024, 17, 1229

Discerning rise time constants to quantify charge carrier extraction in perovskite solar cells†

Sandheep Ravishankar,^a Lennard Kruppa,^a Sandra Jenatsch,^b Genghua Yan^a and Yueming Wang^a

Science

TECHNICAL COMMENTS

Cite as: S. Ravishankar *et al.*, *Science*
10.1126/science.abd8014 (2021).

Comment on “Resolving spatial and energetic distributions of trap states in metal halide perovskite solar cells”

Sandheep Ravishankar¹, Thomas Unold², Thomas Kirchartz^{1,3*}

PRX ENERGY 2, 033006 (2023)

How Charge Carrier Exchange between Absorber and Contact Influences Time Constants in the Frequency Domain Response of Perovskite Solar Cells

Sandheep Ravishankar^{a,1,*} Zhifa Liu^{a,1} Yueming Wang,¹ Thomas Kirchartz^{a,1,2} and Uwe Rau^{a,1}

PRX ENERGY 1, 013003 (2022)

Multilayer Capacitances: How Selective Contacts Affect Capacitance Measurements of Perovskite Solar Cells

Sandheep Ravishankar,^{1,*} Zhifa Liu,¹ Uwe Rau,¹ and Thomas Kirchartz^{1,2}



I will lead a new junior research group at Forschungszentrum Jülich, Germany.

Candidates interested in PhD and postdoctoral positions can contact me at s.ravi.shankar@fz-juelich.de.

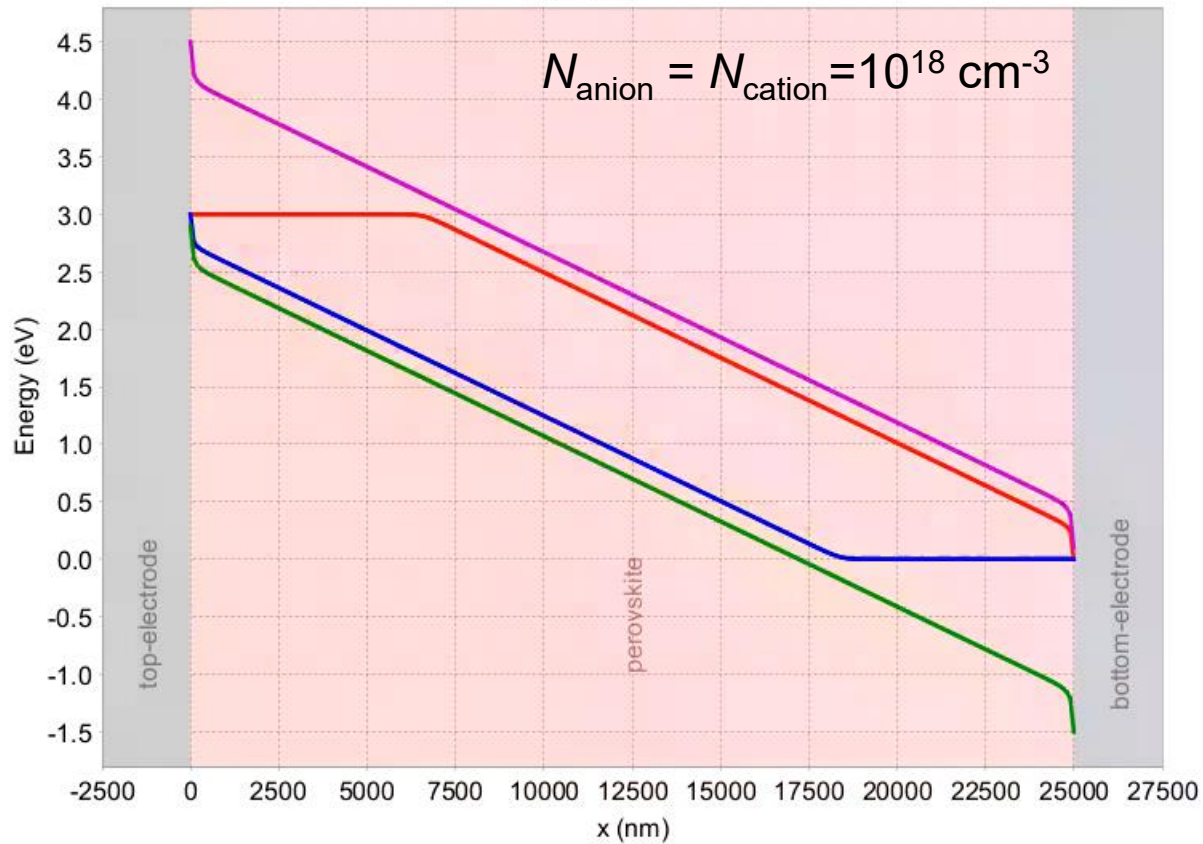
effect of mobile ions

single crystal device – drift-diffusion simulation

Band diagram

Voltage : -3 V

$$N_{\text{anion}} = N_{\text{cation}} = 10^{18} \text{ cm}^{-3}$$



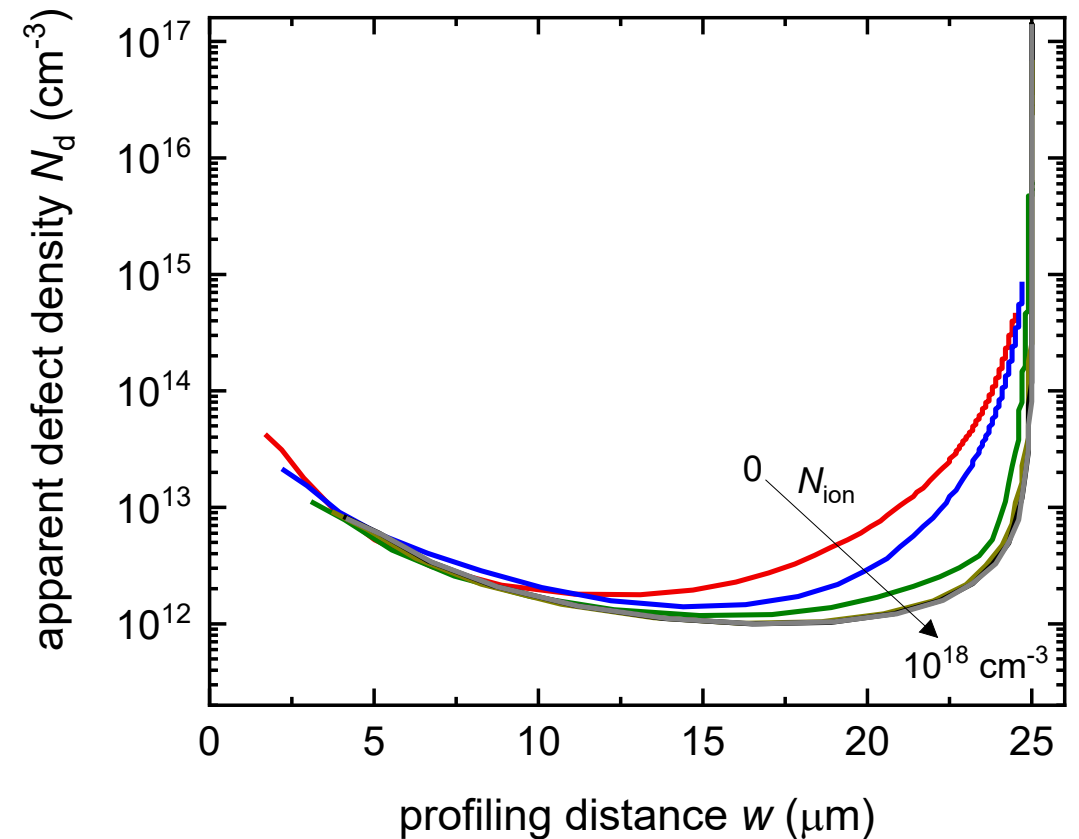
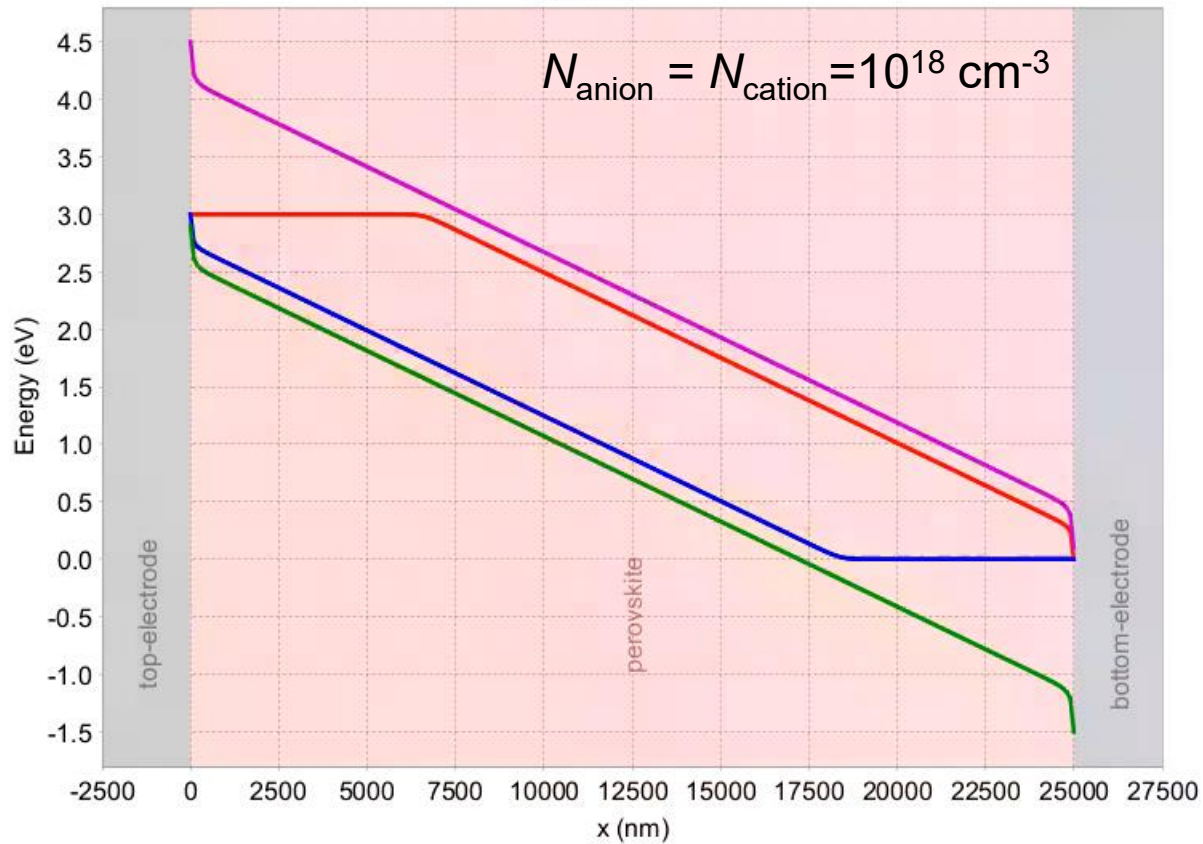
effect of mobile ions

single crystal device – drift-diffusion simulation

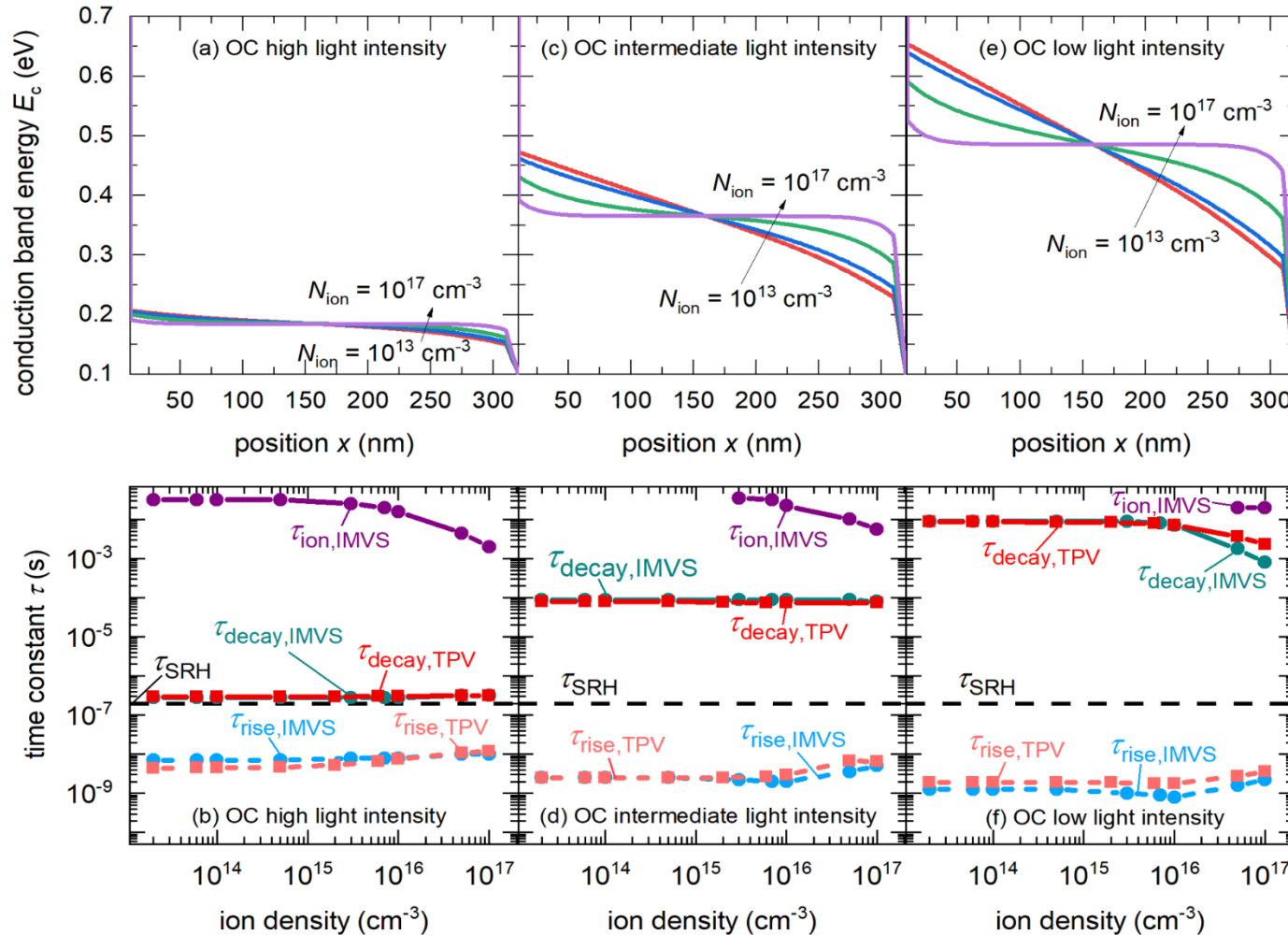
Band diagram

Voltage : -3 V

$$N_{\text{anion}} = N_{\text{cation}} = 10^{18} \text{ cm}^{-3}$$



drift-diffusion simulations

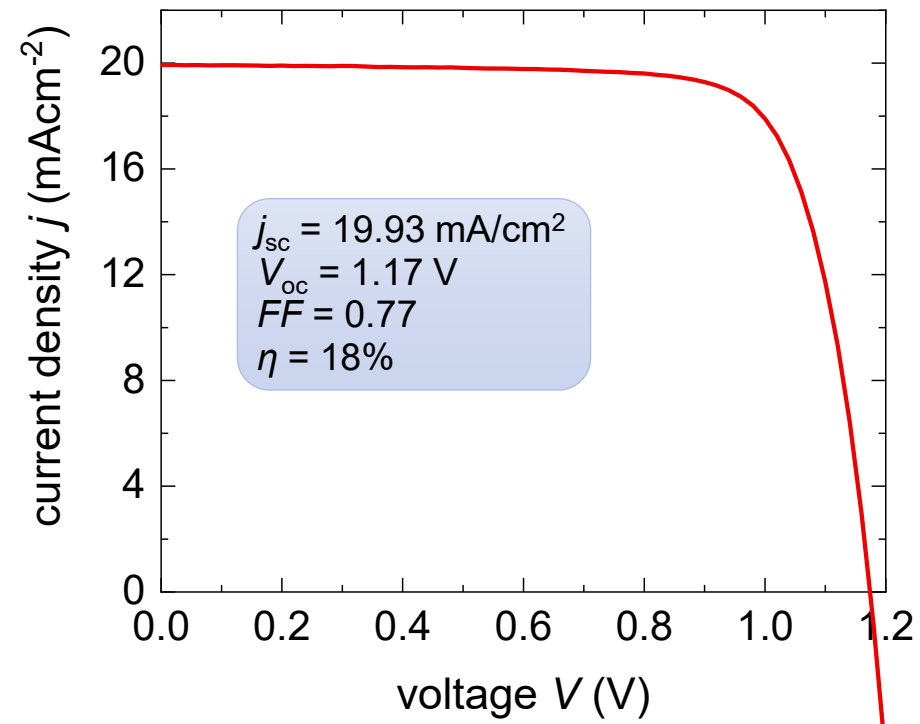


developed analysis using the modified transfer function is valid for devices with mobile ionic densities

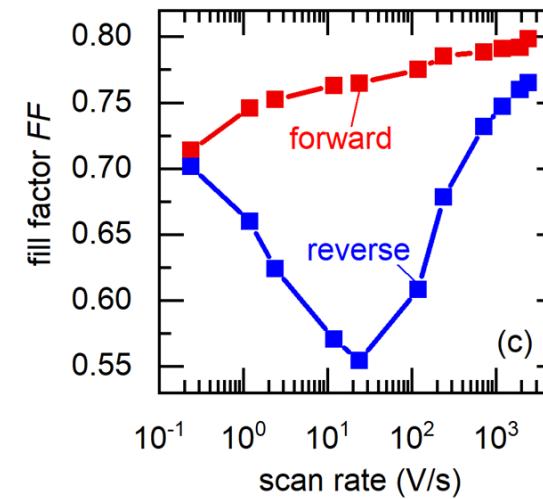
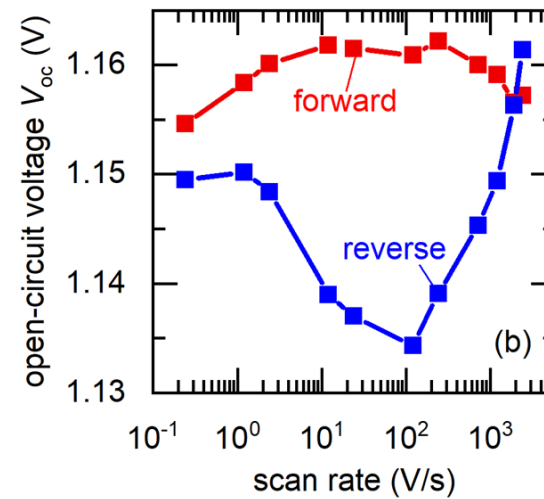
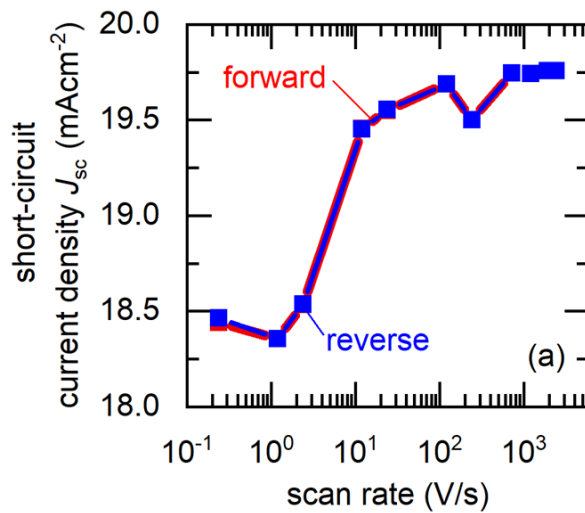
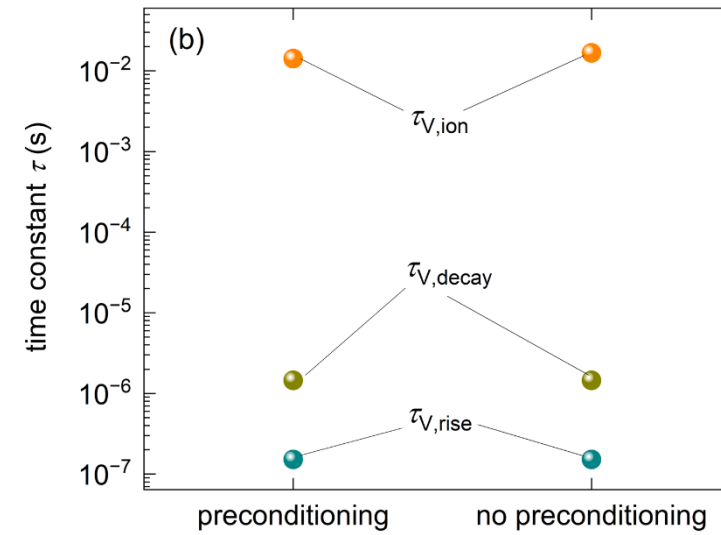
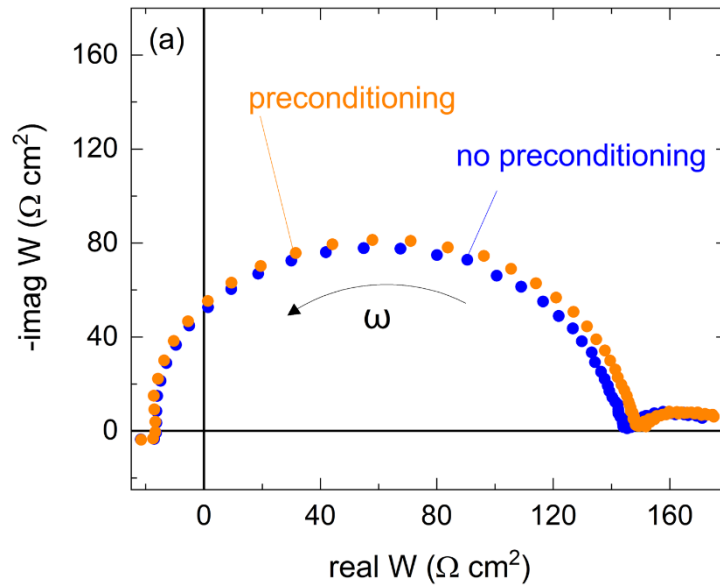
additional time constant at low frequencies due to the slow movement of the ions

application to experimental data

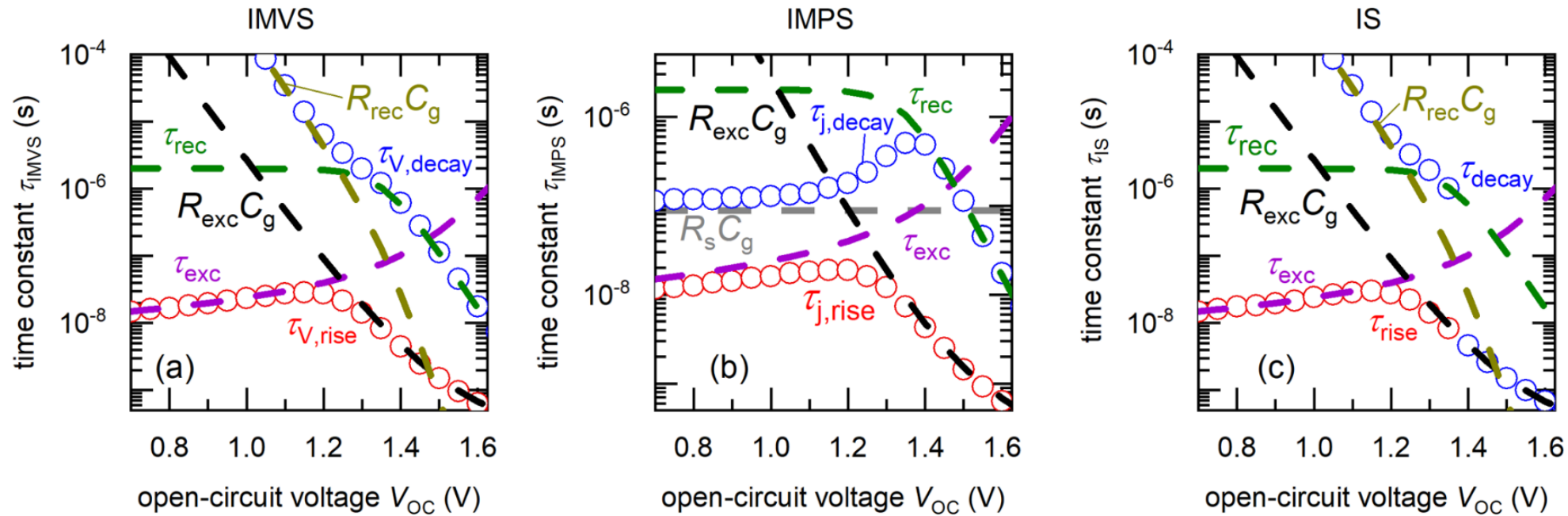
ITO/SAMs/PTAA/Cs_{0.05}FA_{0.8}MA_{0.15}PbI_{2.25}Br_{0.75} (1.68 eV)/C₆₀/BCP/Ag devices



ionic influence on measured spectra



predicted time constants

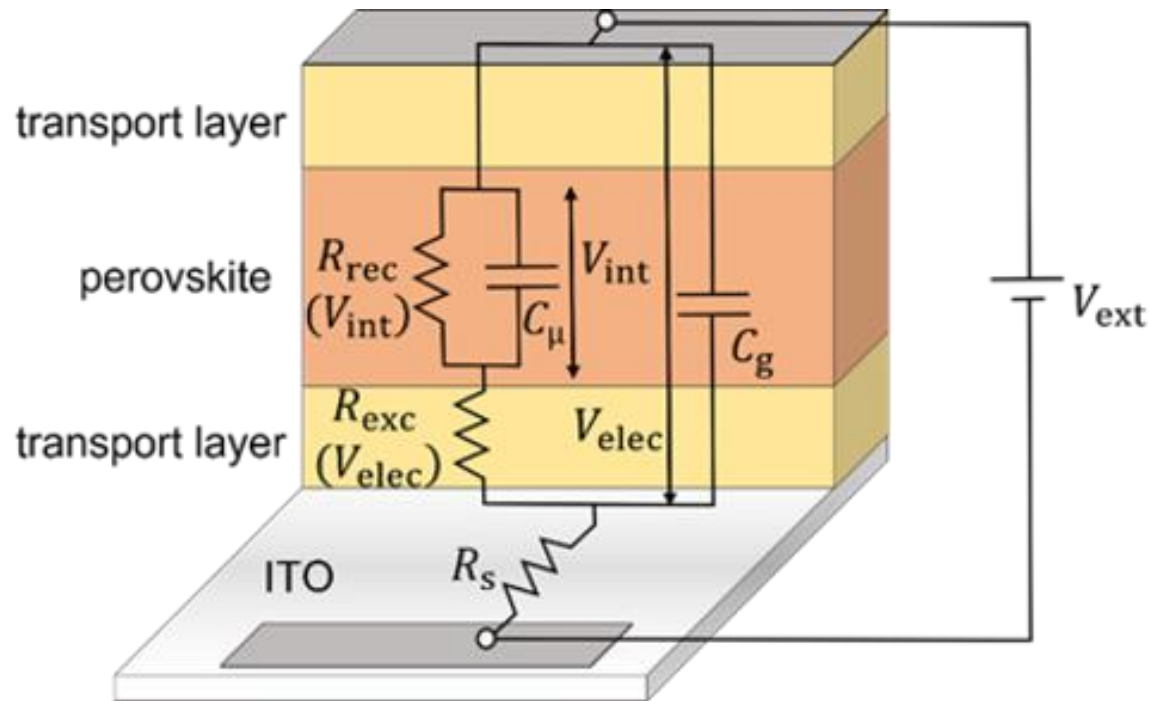


different time constants expressed due to the voltage dependence of resistances and capacitances

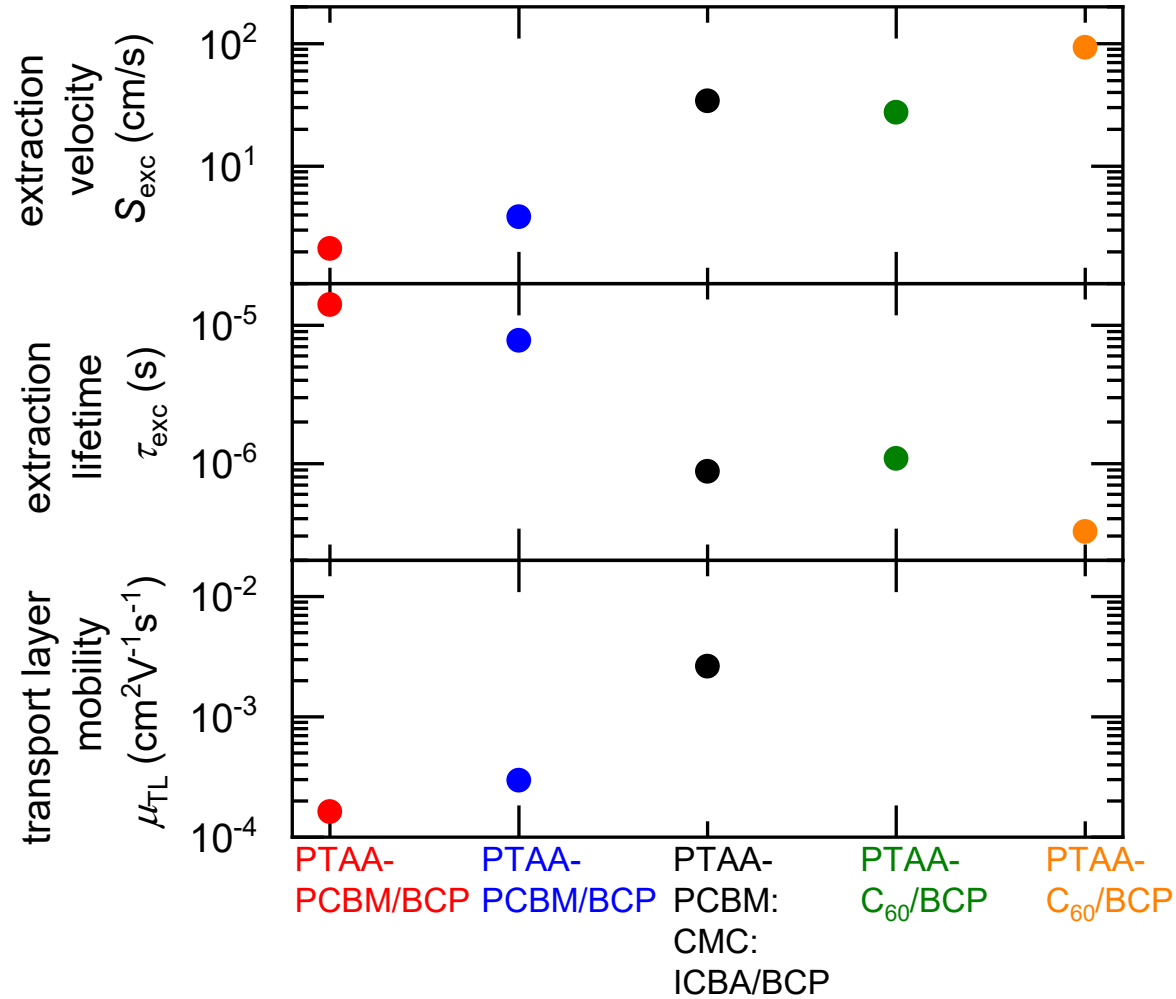
rise time constants generally correspond to charge extraction

decay time constants generally correspond to recombination or R_sC_g attenuation

derived equivalent circuit



accounts for effects related to the difference between the internal voltage V_{int} (quasi-Fermi level splitting) and the external voltage under illumination



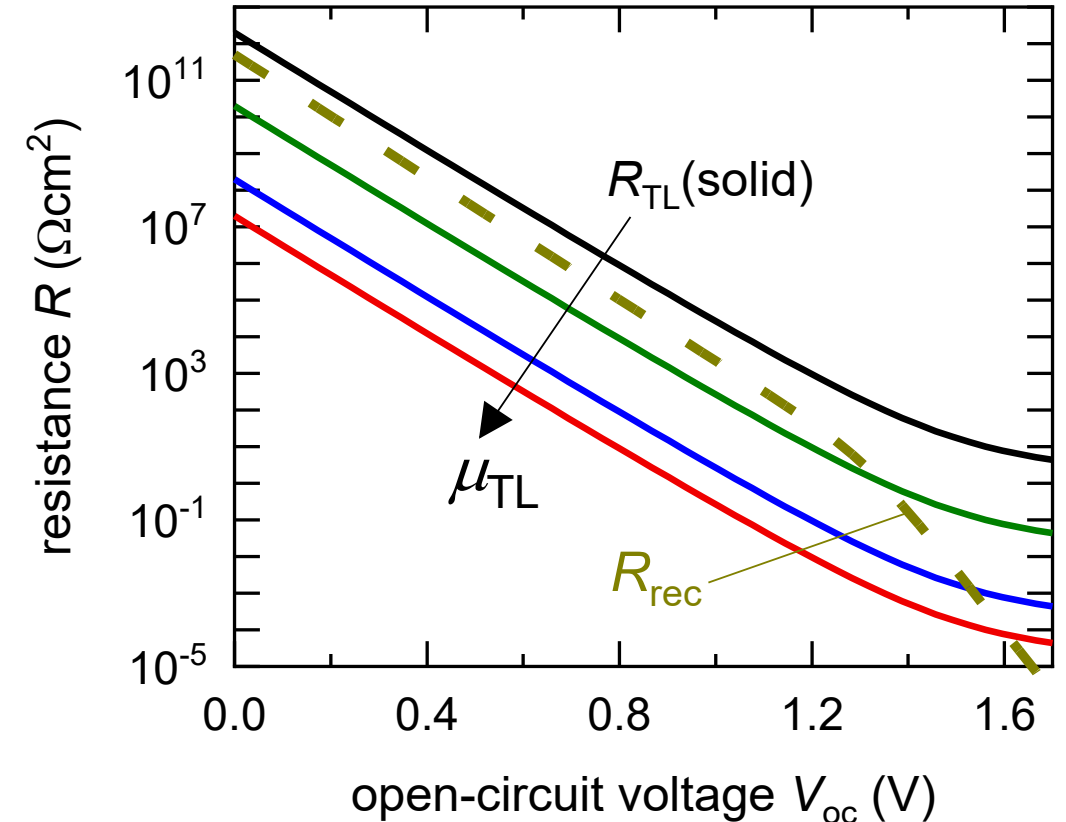
transport layer mobilities between $10^{-4} - 3 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ calculated for PTAA-based PSCs

recombination resistance

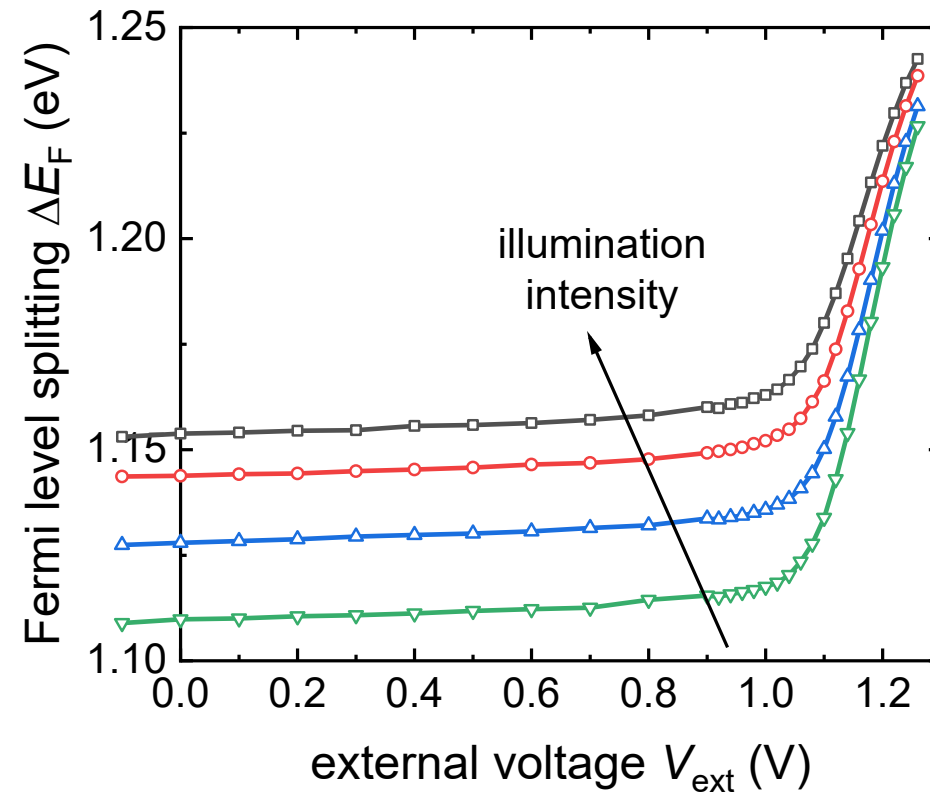
$$R_{\text{rec}} = \left(\frac{1}{R_{\text{rec,SRH}}} + \frac{1}{R_{\text{rec,rad}}} \right)^{-1}$$

transport layer resistance

$$R_{\text{exc}} = \frac{2k_{\text{B}}T}{q^2 n_{\text{i}} S_{\text{exc}}} \exp\left(\frac{-qV_{\text{elec}}}{2k_{\text{B}}T}\right)$$



the internal and external voltage



$$j_{rec}(V_{ext}) = j_{rec,0} \exp\left(\frac{\Delta E_F(V_{ext})}{n_{id} k_B T}\right)$$

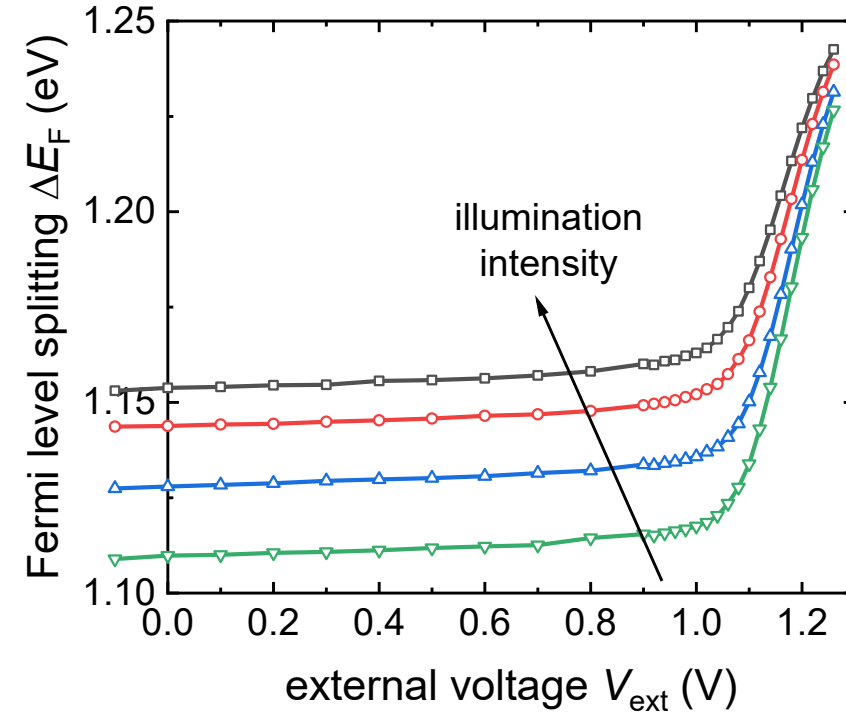
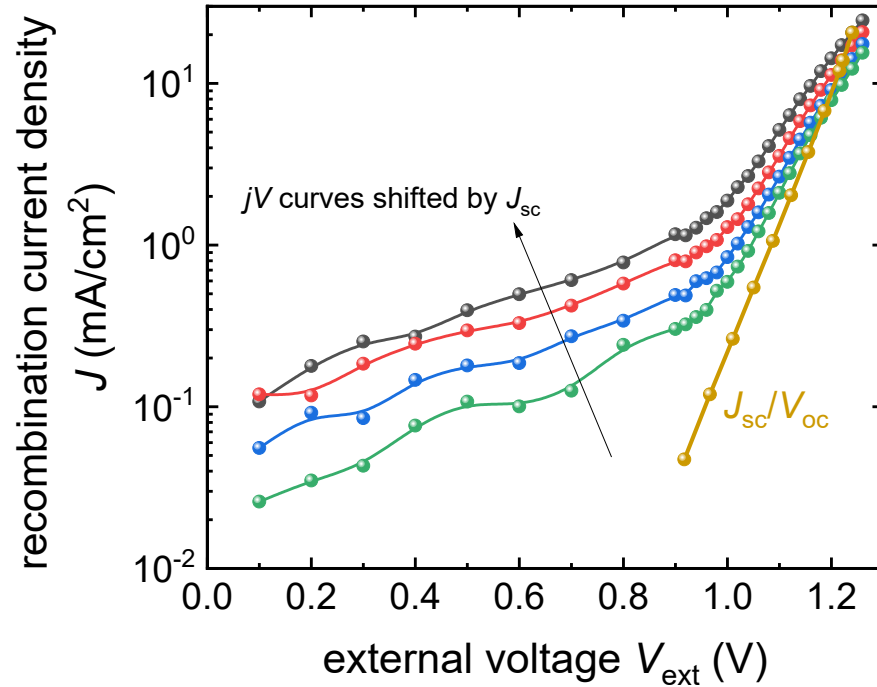
$$j = j_{sc} - j_{0,sat} \left(\exp \left(\frac{qV_{ext}}{n_{id}k_B T} \right) - 1 \right)$$

assumptions

quasi-Fermi level splitting is equal to the external voltage, with and without illumination

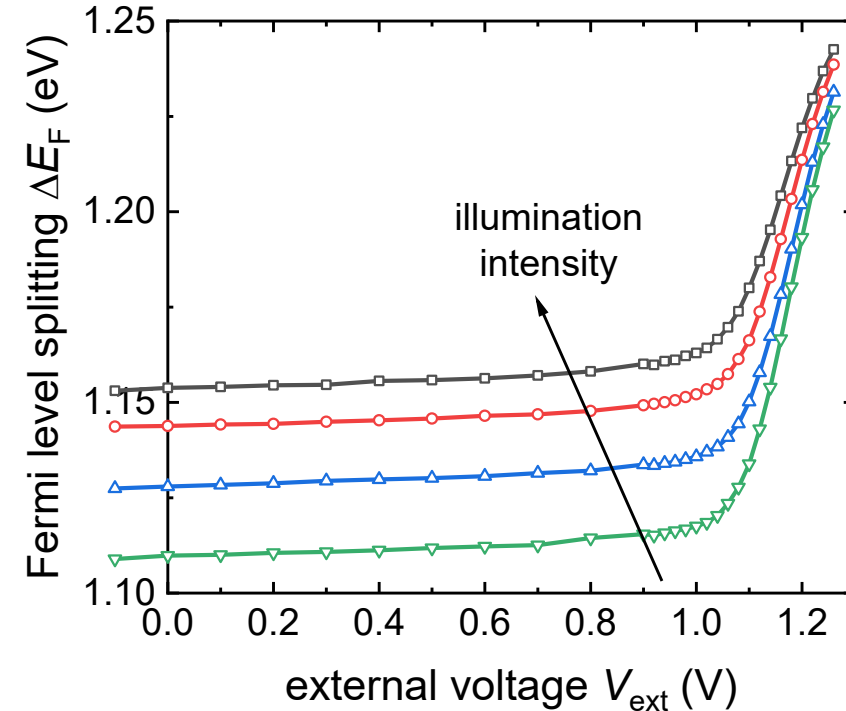
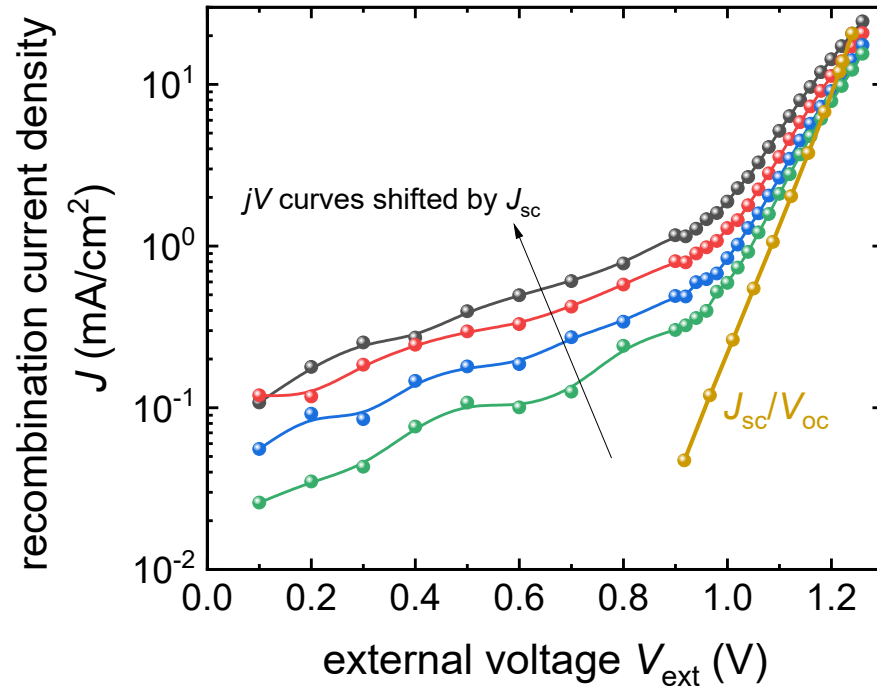
current due to photogeneration of charge carriers can be superimposed on the dark jV curve

j-V curve



$$j = j_{\text{sc}} - j_{0,\text{sat}} \left(\exp \left(\frac{qV_{\text{ext}}}{n_{\text{id}}k_{\text{B}}T} \right) - 1 \right)$$

j-V curve with influence of transport layers



accounts for recombination losses
at all points of the jV curve

$$j = qS_{\text{exc}}n_0 \left[\exp\left(\frac{qV_{\text{int}}}{n_{\text{id}}k_{\text{B}}T}\right) - \exp\left(\frac{qV_{\text{ext}}}{n_{\text{id}}k_{\text{B}}T}\right) \right]$$