Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

for

Deciphering capacitance frequency technique for performance limiting defect state parameters in energy harvesting perovskites

Vikas Nandal,[*a,b] Sumanshu Agarwal,[*c] and Pradeep R. Nair[*b]

[a] Global Zero Emission Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan.

[b] Department of Electrical Engineering, Indian Institute of Technology Bombay, Mumbai-400076, Maharashtra, India.

[c] Department of Electronics and Communication Engineering, Institute of Technical Education and Research, Siksha 'O' Anusandhan (Deemed to be) University, Bhubaneswar, Odisha—751030, India.

[*] Email: nk.nandal@aist.go.jp, sumanshuagarwal@soa.ac.in, prnair@ee.iitb.ac.in

Table S1. Material parameters employed to study capacitance frequency technique in perovskite-based PIN device.

Parameters	Numerical values
Effective density of states for conduction/valence band, $N_{c,v}$	$10^{20}\ cm^{-3}$
Charge carrier mobility, μ	$0.2\ cm^2V^{-1}s^{-1}$
Charge carrier life time, τ	$3\ \mu s$
Band gap, E_g	$1.55\ eV$
Dielectric constant	4
Conduction (or valence) band offset at HTL(or ETL)/perovskite interface	$1\ eV$
Valence (or conduction) band offset at HTL(or ETL)/perovskite interface	$0\ eV$
Doping density	$10^{18}cm^{-3}$ p-type in HTL, n-type in ETL
Trap energy, E_t	0.3-0.7 eV
Trap density, N_t	(3 to 10) $\times 10^{16}\ cm^{-3}eV^{-1}$
Gaussian dispersion factor, σ	$0.11\ eV$
Attempt to escape frequency, f_{AEF}	$3 \times 10^{11}\ Hz$

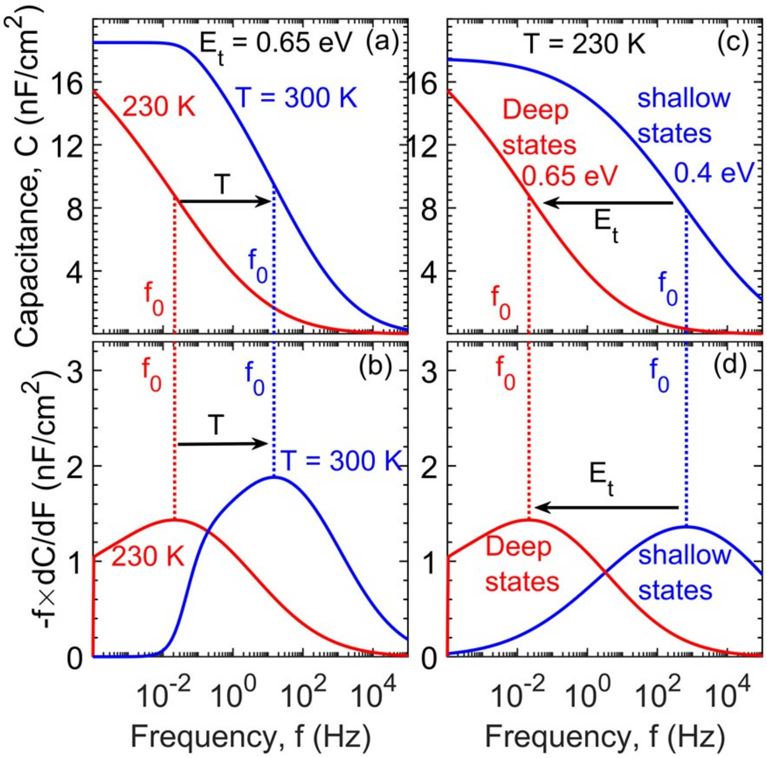

Figure S1. Influence of (a, b) temperature T and (c, d) trap energy E_t on the capacitance C frequency f and $-fdC/df$ frequency characteristics of perovskite-based PIN devices with trap density $N_t = 5 \times 10^{16}\ cm^{-3}eV^{-1}$. In panel (a), for deep trap states $E_t = 0.65\ eV$, the increase in capacitance with the temperature is originated from the thermal energy induced increased de-trapping response of the trapped charges with the modulating signal frequency f. As a result, in panel (b), the characteristic frequency f_0 (at maximum $-fdC/df$) increases with the increase of temperature. Besides temperature, in panels (c, d), such enhancement effects are obtained for shallow trap states ($E_t = 0.4\ eV$) located close to the valence energy band in comparison to deep trap states ($E_t = 0.65\ eV$).

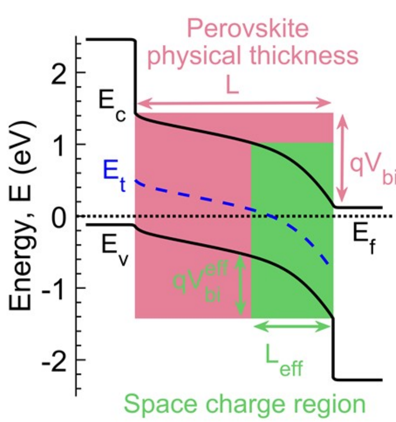

Figure S2. Energy band diagram of perovskite-based PIN device. The trap density $N_t = 5 \times 10^{16} cm^3 eV^{-1}$ with gaussian distribution is located at an energy E_t = 0.65 eV above valence energy band E_v. The trapped negative charges close to and below Fermi-energy level create parabolic energy bands in space charge region (SCR). The effective length L_{eff} and built-in voltage V_{bi}^{eff} of SCR are less than the values (L; V_{bi}) across physical thickness of perovskite layer.

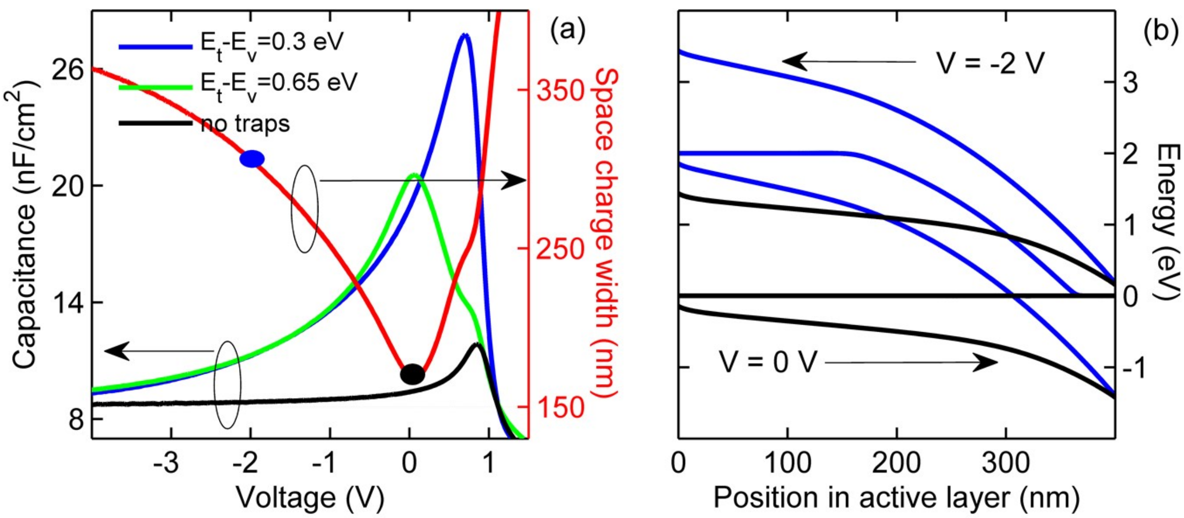

Figure S3. (a) Effect of trap density N_t (present at trap energy E_t) on capacitance-voltage (CV) characteristics (on the left axis) and variation of extracted effective length or space charge width $L_{eff} = \epsilon / C$ with voltage at trap energy $E_t = 0.65\ eV$. (b) Energy band diagram in the perovskite layer at voltage $V = -2, 0\ V$. CV characteristics follows Mott-Schottky behavior, whereas the effective length having parabolic energy bands increases with the decrease of voltage.

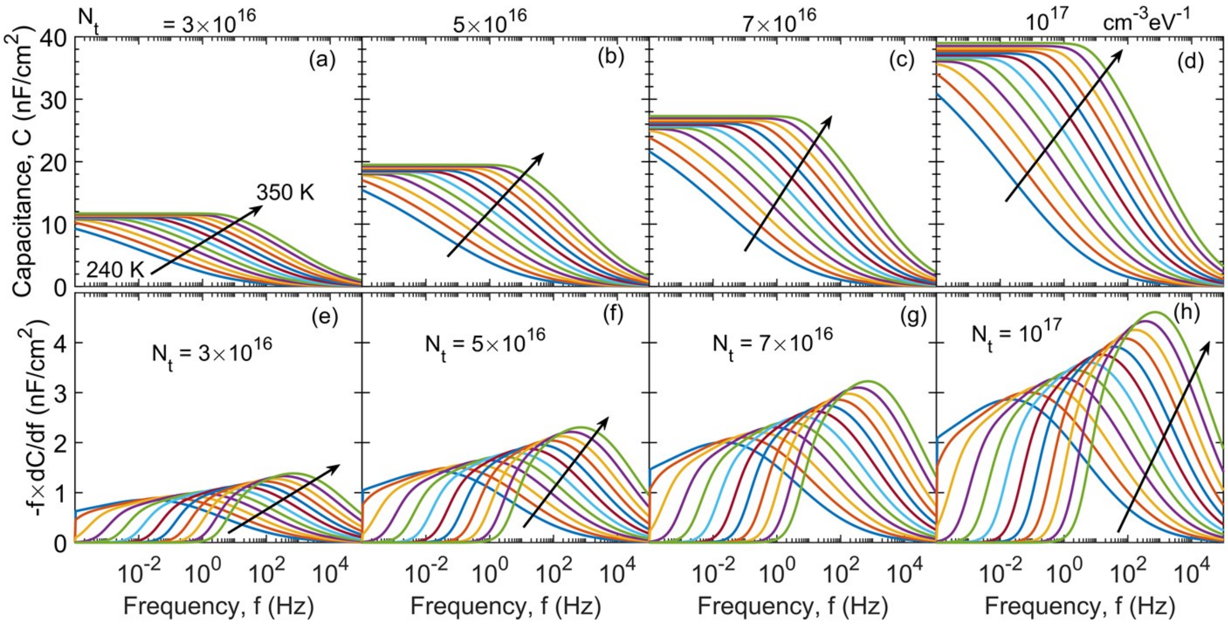

Figure S4. Capacitance frequency technique (CFT) analysis of perovskite-based PIN devices. (a-d) Computed capacitance frequency CF cures, and (e-h) $-fdC/df$ *vs.* frequency f characteristics at temperature T (= 240 to 350 K in steps of 10 K) for various input trap density N_t located at deep trap energy $E_t = 0.65\ eV$ from valence energy band. Increase in N_t primarily leads to the increase in the magnitude of the capacitance C and $-fdC/df$, however, does not exhibit a change in frequency f_0 (corresponding to maximum $-fdC/df$) at a fixed T.

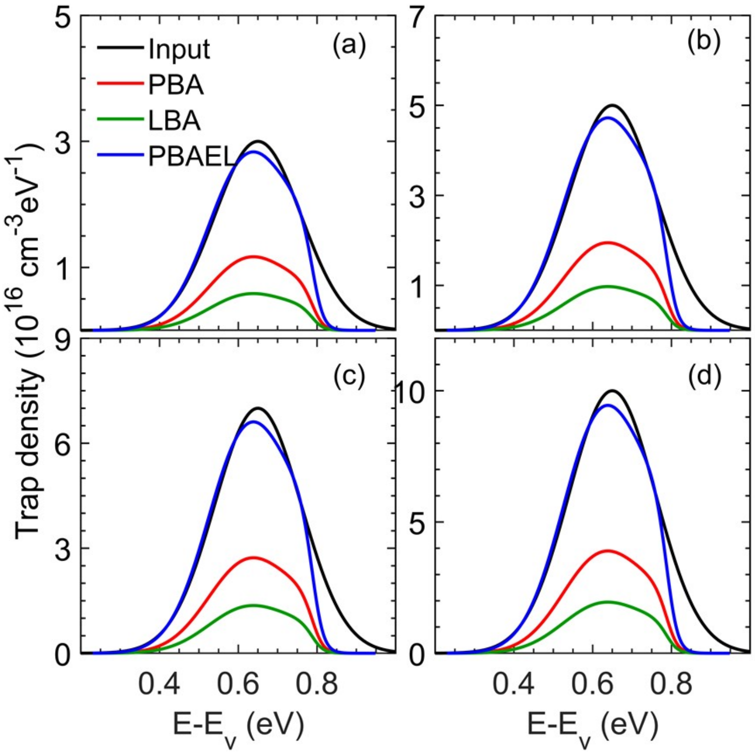

Figure S5. Predicted trap states distribution from capacitance frequency technique of perovskite-based PIN devices. Extracted trap states distribution using different models (*i.e.*, developed PBAEL, previous PBA, and LBA models). The black lines represent the actual input of gaussian trap state distribution in the perovskite layer at trap energy $E_t = 0.65\ eV$. PBAEL model accurately estimates the trap state distribution, whereas the exiting models of PBA and LBA provide the underestimated values.