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

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Ni et al. (Research Articles, 20 March 2020, p. 1352) report bulk trap densities of \(10^{11}\) cm\(^{-3}\) and an increase in interfacial trap densities by one to four orders of magnitude from drive-level capacitance profiling of lead halide perovskites. From electrostatic arguments, we show that the results are not trap densities but are a consequence of the geometrical capacitance and charge injection into the perovskite layer.

Despite the excellent optoelectronic properties of lead-halide perovskites, efforts to better understand the details of the remaining losses due to nonradiative recombination via defects are crucial to further improve the performance of photovoltaic or light-emitting devices. One method that can determine the energetic depth of a trap and its spatial position is the so-called drive-level capacitance profiling (DLCP) method. Ni et al. (1) recently applied this method to halide perovskite solar cells to resolve bulk trap densities as low as \(~10^{11}\) cm\(^{-3}\) and interfacial trap densities that increase by one to four orders of magnitude from bulk values [see figure 3A of (1)]. However, a charge density can only be detected in capacitance measurements if it affects the electrostatic potential, which requires either sufficiently high charge densities, low permittivities, or sufficient thicknesses (2). Using basic electrostatic arguments, we show that capacitance-based methods cannot resolve the charge densities observed in (1), except for the measurement shown in their figure 1E. We show by numerical simulation that perovskite solar cells without any defects or dopant atoms yield a response that closely resembles the one in (1), indicating a universal threshold value below which the response cannot be considered to originate from a density of defects or dopants.

The inherent assumption required to obtain spatial information in capacitance profiling methods such as capacitance-voltage (CV) and DLCP measurements is the existence of a space-charge region of width \(w\) generated by a charge density \(N_d\) (dopant or trap densities), within the device of thickness \(d\), that can be modified by the applied voltage \(V\). Upon applying a perturbation, a response is obtained from the edge of the depletion region or from a density of emission-limited traps located at the junction transition region (3). Although DLCP is not a small-perturbation technique like a CV measurement, the electrostatic origin of the response is identical. Indeed, the two techniques often yield similar results, especially at low frequencies where the deep traps respond (3).

We use this property to illustrate the limitations of the DLCP technique in resolving charge densities, from numerical simulations of CV measurements of perovskite solar cells using SCAPS (4). A common representation is the doping density profile, which is a plot of \(N_{d0}(w) = -2(dC^2/dV)\(1/q\) versus profiling distance \(w = \varepsilon_r\varepsilon_0/C(V)\), where \(C\) is the capacitance per unit area (F cm\(^{-2}\)), \(\varepsilon_r\) and \(\varepsilon_0\) are the relative permittivity of the perovskite and permittivity of free space, respectively, and \(q\) is the elementary charge. A simulated doping profile for a dopant- and trap-free perovskite solar cell (Fig. 1A; parameters and band diagram in table S1 and fig. S1) is shown for the same thicknesses used in figure 3A of (1). The apparent doping profile is U-shaped and is nearly identical to the spatial trap density profile reported in figure 3A of (1). A similar effect is observed in Fig. 1B for an intrinsic dopant- and trap-free thin film solar cell, although the apparent doping densities are a few orders of magnitude higher, again in agreement with the values reported in (1).

These doping profiles can be understood from the relation between a Mott-Schottky plot (\(C^2\) versus \(V\)) and a doping profile (fig. S2). The increases in apparent dopant density at the interfaces are simply the plateaus at low and high forward bias of the Mott-Schottky plots (fig. S3), whereas the apparent doping density in the bulk corresponds to the linear apparent Mott-Schottky regime. Such a shape of the Mott-Schottky profile is actually a fundamental response caused by a geometrical electrode
capacitance combined with charge injection. Charge injection at forward bias in a diode typically leads to an exponentially voltage-dependent capacitance (see supplementary materials for details). If we connect this capacitance in parallel to a geometric capacitance [i.e., $C = C_g + C_0 \exp(qV/mk_BT)$, where $k_BT$ is the thermal voltage and $m$ is a factor that controls the slope of $C$ versus $V$], the shape of the doping profiles can be analytically calculated (see supplementary materials).

If the doping and trap densities are too small to affect the electric field of the perovskite layer of thickness $d$, the condition $w \leq d$ is not satisfied. For example, for the lowest reported bulk trap densities of $\sim 10^{11}$ cm$^{-3}$ in $\sim 39$-μm-thick perovskite layers in (1), the theoretical space-charge layer width at the onset of the linear Mott-Schottky region would be $w = 88.5$ μm—that is, larger than the crystal thickness. In such situations, the geometric and injection capacitances dominate the response and yield a minimum charge density (derived in supplementary materials) given by

$$N_{d,\text{min}} = \frac{27mk_BT\epsilon_r\epsilon_0}{4q^2d^2}. \tag{1}$$

This value (shown in Fig. 1C) sets the plateau region of the doping profile, and only measured charge densities greater than this limit (green shaded region) can be considered as a response from doping or from charged defects. Note that the condition $N_d \gg N_{d,\text{min}}$ holds for any measurement frequency (see supplementary materials). If the probed carrier or trap density does not comply with $N_d \gg N_{d,\text{min}}$, the capacitance response must arise from charge injection likely combined with a capacitive response of the transport layers (see supplementary materials). Because the minimum charge density is inversely proportional to the square of the thickness of the device, intrinsic thin films will always show larger apparent doping and trap densities than bulk single crystal films, as was observed experimentally in figure S10B of (1).

As mentioned above, the apparent rise in interfacial charge densities is a direct consequence of charge injection, which is analytically described by $N_d(w) = mk_BT\epsilon_r\epsilon_0/q^2w^2$ (see supplementary materials) and is indeed universally observed for DLCP or CV measurements of several photovoltaic technologies (Fig. 2). Therefore, only charge densities in the plateau region of the doping profile [such as seen in figure 1E of (1)] should be considered as representing dopant/trapped charge densities if they are larger than $N_{d,\text{min}}$.

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SUPPLEMENTARY MATERIALS
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Fig. 1. Doping profiles and minimum charge densities required for resolution in bulk single crystal and polycrystalline thin film trap-free, dopant-free perovskite solar cells. (A) Simulated spatial doping profiles at $10^3$ Hz of a p-i-n–type PTAA (10 nm)/perovskite/PCBM (25 nm) solar cell for the same thicknesses of the bulk perovskite layer as used in figure 3A of (I). Arrow indicates reduction of apparent bulk charge (dopant or trap) densities with increasing thickness. The profile is identical to figure 3A of (I) even in the absence of any dopant or trap densities in the model. (B) Different thicknesses between 300 and 800 nm representative of perovskite thin films. Arrow indicates apparent reduction of bulk charge densities with thickness. (C) Minimum charge densities (dopant or trap) that will be observed in a capacitance-voltage measurement ($m = 2$ is assumed) for different thicknesses and permittivities typical of perovskite (olive) and silicon or organic (cyan) solar cells, in comparison with measured minimum charge densities reported for bulk single crystal and polycrystalline thin films in (I). The green region represents charge densities that are experimentally accessible for the perovskite solar cell.

Fig. 2. Universal rise in apparent interfacial charge densities due to charge injection. (A and B) Some reported spatial trap profiles shown with linear (A) and logarithmic (B) horizontal axis obtained from DLCP and CV measurements for different solar cell technologies such as amorphous hydrogenated silicon (a-Si:H) (5), copper indium gallium selenide [CuIn$_{x}$Ga$_{1-x}$Se$_{2}$ (CIGS)] (6, 7), methylammonium lead iodide perovskite (I), cadmium telluride (CdTe) (8), and an 8-μm-thick p-i-n–type perovskite solar cell simulated using SCAPS. Also plotted is the analytical formula (with $m = 1.5$ and $\varepsilon_r = 30$) derived by considering a geometric capacitance in parallel with an exponential injection capacitance (see supplementary materials). The capacitance related to injection of charge at forward bias causes an apparent rise in the interfacial charge densities at the lowest profiling distances [left side of U-shaped profile in (A)] that can erroneously be interpreted as trap densities. The geometric capacitance gives the corresponding rise in interfacial charge densities at maximum profiling distances [right side of U-shaped profile in (A)]. The universality in the doping profiles of different types of solar cells at forward bias (B) arises from the injection capacitance.