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

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Ravishankar et al. claimed that drive-level capacitance profiling (DLCP) cannot resolve trap density in perovskites of given thickness. We point out that the trap densities derived by DLCP are from the differential capacitance at different frequencies; thus, the background charges caused by diffusion and geometry capacitance have been subtracted. Even for the nondifferential doping analysis, the contribution from diffusion capacitance is negligible and that from geometry capacitance is excluded.

In their Comment, Ravishankar et al. (1) derived an apparent carrier density distribution in semiconductor devices based on a capacitance model by assuming the combination of geometrical capacitance ($C_g$) and diffusion capacitance ($C_d$) as the dominant capacitance for semiconductor devices:

$$C = C_g + C_d \exp \left( qV / m k_B T \right)$$

(1)

where $q$ is elementary charge, $V$ is the dc bias, $m$ is the ideality factor [which was assumed to be 2 for the interpretation of Fig. 1C in (1)], $k_B$ is the Boltzmann constant, and $T$ is temperature. This is the equation upon which all their analysis is based. The authors derived the carrier density by assuming that this apparent (total) capacitance under forward bias follows the equations developed for reverse bias capacitance in a diode [eq. S8 in (1)], where the geometric and diffusion capacitance were not separated from the junction capacitance and were interpreted as part of the junction capacitance with the capacitance-voltage (CV) method. It is unknown whether this assumption stands, because neither geometrical nor diffusion capacitance is a function of carrier concentration. It is not appropriate to directly use the charge density from this CV method (small perturbation) to represent the carrier density from DLCP measurement (large perturbation), because studies have shown that the doping and charge densities were very likely to be skewed to larger values with the CV measurement if substantial densities of deep trap states exist within the depletion region (2). Even in (3), the experimental results showed that the CV measurement actually overestimated the free carrier density in the CuInSe$_2$ solar cell relative to the DLCP results by several times.

Nonetheless, even under the framework in which carrier density and profile distance directly from CV measurement are used to represent those from DLCP measurement, the following analysis shows that the geometry and diffusion capacitance have no impact on the measurement of charge trap densities by DLCP. Equation 1 predicts that carrier density is independent of applied ac frequency ($\omega$); however, the experimental results in (4) showed a substantial frequency-dependent carrier distribution. The frequency-dependent capacitance is a critically important characteristic of charge traps and allows for the determination of their density with the DLCP method. Without a frequency-dependent carrier density, the traps would not show a trap-energy resolution as shown in figure 3 of (4). The trap density distributions shown in (4) were derived from the difference of the carrier densities at different ac frequencies under the same dc biases. The calculated carrier or trap density would be zero by the DLCP method if there is no frequency-dependent capacitance. In other words, the charge density derived from Eq. 1 does not show up as a background carrier density in the trap profiling derived from DLCP, and thus does not dismiss the application of DLCP in characterizing the trap densities.

Equation 1 does not represent the capacitance of a semiconductor device because it has a bias-independent constant junction capacitance of a p-n junction and also neglects the frequency dependence of $C_d$, although we understand that the trapping and detrapping of charge-
induced capacitance was omitted from this equation on purpose. The dependence of $C_d$ on $V$ and ac frequency $\omega$ of a typical $n^+ - p$ junction is reported in (5). As shown in the supplementary materials, this constraint means that Eq. 1 applies only at low $\omega$. At high $\omega$, the contribution of $C_d$ to $C$ reduces with a relationship of $C_d \propto \omega^{-0.5}$, which indicates that $C_d$ is less important at higher $\omega$. Therefore, the contribution of $C_d$ to the measured doping (not trap) density is very small at high $\omega$.

To verify whether $C_d$ dominates $C$ at large $V$ in perovskite solar cells, we measured the $C$-$V$ curves of a silicon diode (p-n junction) and perovskite single crystal and thin film solar cells at 62 kHz (Fig. 1A). The $C$-$V$ of the silicon diode follows the relationship between $C_d$ and $V$ for $V \gtrsim 0.4$ V (see supplementary materials), although the $C$-$V$ response of the perovskite solar cell at large $V$ did not follow Eq. 1. Because $C_d$ is related to both $V$ and $\omega$ (see supplementary materials), we further checked whether $C$ was dominated by $C_d$ at large $V$ over a wide range of $\omega$. The measured $C$-$\omega$ curves and the analytically calculated $C_{r\omega}$ plots are shown in Fig. 1, B, C, and E. The parameters used for the calculation of the $C_{r\omega}$ curves are summarized in table S1. Again, the calculated $C_{r\omega}$ curves fit well for the Si diode in the low ac frequency region ($\omega\tau \ll 1$) where $C_d$ is independent of $\omega$ (see supplementary materials), and $C_d$ is proportional to $\omega^{-0.5}$ at high ac frequencies ($\omega\tau \gg 1$) (where $\tau$ is the minority carrier lifetime) (Fig. 1B).

In contrast, the calculated $C_d$ values are 5 and 11 orders of magnitude smaller than the measured capacitance at large $V$ over the wide range of $\omega$ for the thick single crystal and thin film perovskite solar cells, respectively (see supplementary materials). This difference is mainly attributed to the low minority carrier density in perovskites because of the self-doping of perovskite materials, which typically have a majority carrier density of $10^{10}$ to $10^{15}$ cm$^{-3}$ $(6-9)$. Therefore, the $C_d$ should be negligible in perovskite solar cells for $V$ between 0 and 0.9 V adopted for the carriers density profiling in experiment. In this case, although the carrier densities calculated by the CV method have a U-shape similar to that measured by DLCP, it requires a substantially larger $V$ of 1.0 to 1.6 V to complete the U-shape curve (fig. S1), which does not agree with the experimental data (0.2 to 0.9 V) in (4).

The measured $C$ at different dc biases and frequencies in Fig. 1, C and E, also does not follow the response of $C_d$ with $\omega$ predicted by eqs. S1 to S3. The measured $C$ keeps increasing with the decrease of $\omega$ in the low ac frequency region, instead of being a constant. To understand the possible contributions from the charge transport layers to the frequency-dependent capacitance of the perovskite solar cells, as argued by Ravishankar et al., we used the SCAPS software to simulate the $C$-$\omega$ curves of trap-free perovskite solar cells with both charge transport layers (10). As shown in Fig. 1, D and F, the trend of the simulated $C$-$\omega$ curves basically resembles the analytically calculated $C_{r\omega}$ curves, both showing a constant $C$ at $\omega$ below $10^5$ Hz, distinctly different from the $C$-$\omega$ curves measured in experiment. We attribute this difference to the contribution of deep trap states from the junction capacitance. Moreover, even at the plateau region of the measured $C$-$\omega$ curves, $C$ did not increase exponentially with $V$. These results further show that the measured $C$ for perovskite solar cells at forward dc biases was still dominated by junction capacitance and charge trapping and detrapping capacitance. Any further analysis based on Eq. 1 would be inaccurate without taking the junction capacitance into consideration, especially when the doping and trap distributions are not uniform in the perovskite.

Finally, we may also use DLCP to evaluate doping density distribution in semiconductor devices by conducting the measurement at high frequency. An absence of subtraction process imposed the question of whether the measured carrier density is correct. We recently showed that the carrier density measured by DLCP in the perovskite films with thickness of 1 μm changed after aging, and had a lower carrier density ($\sim 3 \times 10^{14}$ cm$^{-3}$) than that calculated by Ravishankar et al. (II), which indicates that $C_d$ still did not dominate. Here we estimated the possible contribution of the $C_d$-caused “interfacial carrier density” to the DLCP measured carrier densities in perovskite solar cells by treating $C_d$ in the same way as we did in DLCP measurement (see supplementary materials) (figs. S2 and S3). The contribution of $C_d$ was clearly negligible because the of high frequency of measurement and small minority carrier density, indicating that the measured interfacial charge densities in perovskite solar cells were not caused by the charge injections. In addition, the influence of $C_d$ on the carrier density measurement is prominent only when the applied bias is more than enough to fully deplete the perovskite layers, which was actually excluded in the carrier density profiling by DLCP measurement (see supplementary materials) (figs. S4 and S5).

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Publication date: 26 February 2021 www.sciencemag.org
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ACKNOWLEDGMENTS
Supported by Center for Hybrid Organic Inorganic Semiconductors for Energy
(CHOISE), an Energy Frontier Research Center funded by the Office of Basic Energy
Sciences, Office of Science within the U.S. Department of Energy. Author
contributions: Z.N. and S.X. carried out the capacitance measurements, Z.N.
performed the SCAPS simulations, J.H. and Z.N. wrote the paper, and all authors
reviewed the paper. Competing interests: The authors declare that they have no
competing interests. Data and materials availability: All data needed to evaluate
the conclusions in the paper are present in the paper and in the references cited.
Additional data related to this paper may be requested from the authors.

SUPPLEMENTARY MATERIALS
science.sciencemag.org/content/371/6532/eabd8598/suppl/DC1

6 August 2020; accepted 25 November 2020
Published online 26 February 2021
10.1126/science.abad8598
**Fig. 1. Contribution of the diffusion capacitance to the total capacitances.** (A) Normalized C-V curves of a Si diode (red), perovskite thin single crystal (PVK crystal) (blue), and polycrystalline thin film (PVK film) (green and khaki) solar cells measured at ac frequency (ω) of 62 kHz. The solid red and orange lines plot the dependence of $C_d$ on $\exp(qV/mk_BT)$ with $m = 1.25$ and $2$, respectively. (B, C, and E) C-ω curves of the Si diode (B), perovskite thin single crystal (C), and perovskite thin film solar cell (E) measured at different dc biases. The dashed lines show the calculated $C_d$ curves with eq. S1 (see supplementary materials). (D and F) SCASP-simulated C-ω curves of a trap-free perovskite thin single crystal (D) and a perovskite thin film solar cell (F).
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Science 371 (6532), eabd8598. DOI: 10.1126/science.abd8598