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Comment on "On accurate capacitance characterization of organic photovoltaic cells" [Appl. Phys. Lett. 100, 213902 (2012)]

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In the 100th volume of APL, the work entitled "On accurate capacitance characterization of organic photovoltaic cells" was published.[1] Its subject does not surprise us, as it reflects problems arising while analyzing small signal spectra of photovoltaic organic devices. The main conclusion roughly states that we should measure parallel capacitance (C_p) within lower frequencies and series capacitance (C_s) within higher ones. This attitude is reasonable; however, the authors do not indicate any limits, which can be important for organic systems and can decrease accuracy. The authors analyze only either C_p or C_s. As guideline they use a criterion of a wide plateau, but the question what can affect the plateau is not put. To answer it we should consider a complete small signal response (SSR). Only this way enables to estimate the effect of particular properties of an organic device (like weak current rectification or contribution of series resistance) on capacitance characterization.

We need to comment on Ref. 1 due to another reason. The authors illustrate their considerations with several results, also with one our work.[2] Reading our results they have confused imaginary part of capacitance (C'') with real one (C'). *De facto* C', and not C'' as the authors assumed, equals C_p and just C' is shown in Mott-Schottky plot.[2] Therefore, our attitude does just align with Ref. 1, and it is not an example of "improper model usage."

Going from the beginning, the authors state that the equivalent circuit like in Fig. 1 often reflects SSR of organic devices well. According to them, such a circuit can be used for modeling of various devices. For instance, it can be applied for organic-organic heterojunction in both planar and bulk structures, for which the capacitance results from a depletion region. It can be also used for an organic layer without depletion region, for which the capacitance results from geometric capacitance.

Let us look into details of SSR of the circuit in Fig. 1. We denote its parameters as: C_o for capacitance, R_{po} for parallel resistance and R_{so} for series resistance. We use here subscripts "po" and "so" instead of "p" and "s" to recognize clearly parameters of elements of equivalent circuit (R_{po}, R_{so}) and small signal functions, which are measured with LCR bridges (R_p, R_s). If this circuit is appropriate for SSR at certain steady voltages, we are interested in accurate values of C_o, R_{po}, and R_{so}. All LCR bridges can measure module and phase of impedance (i.e., $|Z^*|$ and θ). Real and imaginary parts of impedance ($Z^* = Z' + jZ''$) are calculated as $Z' = |Z^*|\cos(\theta)$, $Z'' = |Z^*|\sin(\theta)$. Other small signal functions, like both parts of admittance ($Y^* = Y' + jY''$) or capacitance ($C^* = C' - jC''$) are calculated as $Y^* = 1/Z^*$, $C^* = 1/(j\omega Z^*)$. If there are circumstances indicating that within a selected frequency range the SSR is strongly determined by a capacitor and a resistor, we can measure C_p and R_p or C_s and R_s. Pay attention that C_p and R_p are calculated from SSR according to $Y^* = 1/R_p + j\omega C_p$, while C_s and R_s according to $Z^* = R_s - j/(\omega C_s)$.

A complete SSR consists of a couple of functions (e.g., Z', Z''). We should analyze both of them to estimate parameters of elements in equivalent circuit. We will analyze complex capacitance, since accurate capacitance characterization was considered in Ref. 1. For our circuit, we have

$$C' = \frac{\left(1 + (\omega C_o R_{po})^2\right) C_o R_{po}^2}{\left(R_{po} + R_{so} + (\omega C_o R_{po})^2 R_{so}\right)^2 + (\omega C_o R_{po}^2)^2}, \quad (1)$$

$$C'' = \frac{\left(1 + (\omega C_o R_{po})^2\right)\left(R_{po} + R_{so} + (\omega C_o R_{po})^2 R_{so}\right)}{\omega\left[\left(R_{po} + R_{so} + (\omega C_o R_{po})^2 R_{so}\right)^2 + (\omega C_o R_{po}^2)^2\right]}. \quad (2)$$

Pay attention that $C' = C_p$, while $C'' = 1/(\omega R_p)$. Fig. 2 shows examples of SSR. All curves were obtained at the same values of C_o and R_{so}, while R_{po} takes various values. Dashed line indicates C_o. For higher values of R_{po}, $C' = C_o$ within lower frequencies, so measuring C_p we obtain directly C_o. For small values of R_{po}, C_p is smaller than C_o. Let us consider why. Check low-frequency limit (LFL) of Eq. (1). We see that

$$\lim_{\omega \to 0} C' = C_o \frac{R_{po}^2}{(R_{po} + R_{so})^2}, \quad (3)$$

which implies $C_p = C_o$ when the ratio R_{so}/R_{po} is much smaller than 1. To estimate whether C_p is accurate value of C_o, we have to extract R_{so} and R_{po}. These values cannot be extracted from the C_p curve, since considering high-frequency limit (HFL) of C'

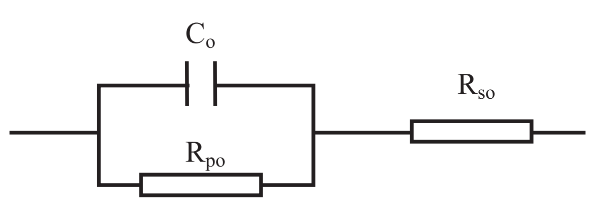

FIG. 1. Equivalent circuit.

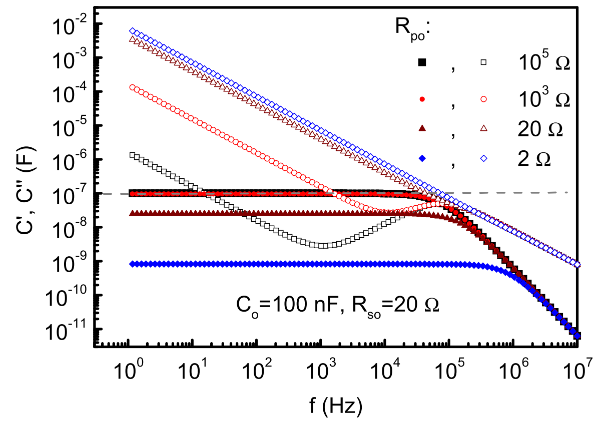

FIG. 2. Real (solid symbols) and imaginary (hollow symbols) parts of capacitance at $C_o = 100$ nF, $R_{so} = 20$ Ω. R_{po} equal: 10^5 Ω (squares), 10^3 Ω (circles), 20 Ω (triangles), and 2 Ω (diamond).

$$\lim_{\omega\to\infty}(\omega^2 C') = \frac{1}{C_o R_{so}^2}, \tag{4}$$

we get LFL and HFL of C′ and three unknown values, C_o, R_{po}, and R_{so}. So, a single curve of C′ can be generated by various sets of C_o, R_{po}, and R_{so}. To get C_o, we must analyze C″ as well. We can extract LFL and HFL of (ωC″) and afterwards C_o according to Eq. (3).

So, even when C_p within lower frequencies does not depend on frequency (a plateau of C_p exists), it does not have to equals C_o. $C_p = C_o$, when $R_{po} \gg R_{so}$. This is often met for inorganic semiconductor diodes at reverse bias. In such cases, the quality factor often takes so high value that it does not matter if we measure C_p or C_s, since for both cases we get the same value. However, for organic devices, we can observe much weaker current rectifications and even at reverse bias an electric current can significantly contribute to SSR. It is worth adding that LFL of Y′ equals a differential direct current conductance of a device.

On the other hand, the accurate value of C_o can be directly measured as HFL of C_s. However, within higher frequencies, resistance (R_s) dominates over absolute value of reactance ($1/\omega C_s$). C_s can be then measured if $1/\omega C_s$ is not too small in comparison with R_s. We do not need very high frequencies, since HFL of C_s can be measured for angular frequencies higher than $1/(C_o R_{po})$.

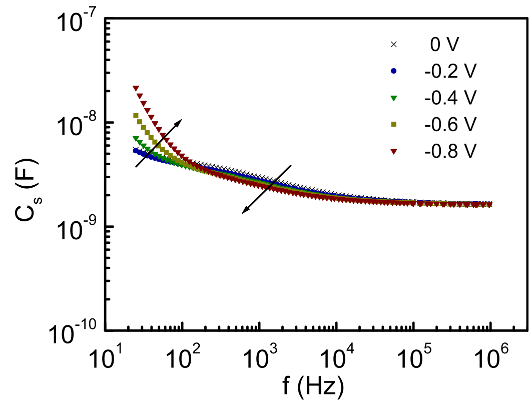

FIG. 3. Series capacitance for reverse bias for the system presented in Ref. 2. Arrows indicate increasing bias.

Finally, we must rectify a mistake which appeared in Ref. 1. We read there that our report "finds an increase in capacitance with reverse bias for frequencies less ca. 400 Hz and draws doubts on MS analysis," however in Fig. 2(b) of Ref. 2 only C″ explicitly increases below 400 Hz and we analyze C′ in Mott-Schottky plot. Nevertheless, Carr and Chaudhary suggest that we should analyze C_p instead of C_s. Respecting that $C' = C_p$, we see that we have just performed analysis of C_p. To be well understood, Fig. 3 shows C_s for the device from Ref. 2. Similarity between our results (Fig. 3 here and Fig. 2(b) in Ref. 2) and results in Fig. 4 of Ref. 1 is noticeable. Therefore, we state that our attitude was the same as that suggested in Ref. 1. On the other hand, our conclusion that from Mott-Schottky plot, we cannot get any unique parameters of depletion region is still valid.

[1] J. A. Carr and S. Chaudhary, Appl. Phys. Lett. **100**, 213902 (2012).
[2] G. Jarosz, J. Non-Cryst. Solids **354**, 4338 (2008).