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Response to "Comment on 'On accurate capacitance characterization of organic photovoltaic cells'" [Appl. Phys. Lett. 102, 076101 (2013)]

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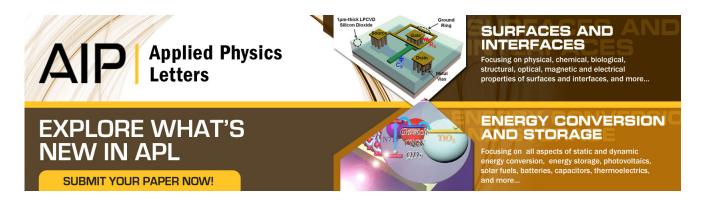
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Response to "Comment on 'On accurate capacitance characterization of organic photovoltaic cells" [Appl. Phys. Lett. 102, 076101 (2013)]

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This Response letter is in reference to the Comment¹ on our Applied Physics Letters publication "On accurate capacitance characterization of organic photovoltaic cells."² The Comment asserts that a confusion in the original article (Ref. 2) relating to a cited work (Ref. 3) has led to a misinterpretation. The Comment further outlines this confusion to ensure clarity, and subsequently supports the general attitude of the original work with a quantitative treatment and an additional data set.

In Response, we must acknowledge that a mistake has been made in interpreting the commenting author's work.³ Specifically, in the cited work (Ref. 3), the real (C') and imaginary (C'') parts of a capacitance measurement were presented. We had interpreted the value of C' to be related to the resistance and C'' to be related to the capacitance. Further, owing to the low frequency behavior of C'' in Fig. 1 of the cited article,³ it seemed quite clear to us that this parameter was representing a series mode measurement, C_s . Specifically, C'' (which we considered the capacitance) increases with an applied reverse bias a low frequencies, a common sign of the series mode parameters becoming invalid. This led us to make the statement that "an increase in capacitance with reverse bias for frequencies less than ca. 400 Hz was seen [in the cited work], and [because of this, the author] draws doubt on MS analysis in their cells." It is typical in the circuit community that the real part of a capacitance measurement denotes the resistance or conductance and the imaginary part denotes the capacitance. For convenience of displaying both parts on the same scale, the real part can be manipulated by a factor of ω ; see Ref. 4, for an example. However, with $Z^* = 1/Y^*$ and $C^* = 1/Y^*$ $(j\omega C^*)$, one has two degrees of freedom when defining C' and C", where $C^* = C' - jC''$. As the commenter points out, the cited work in fact presents C' in representation of C_p and C" for $1/(\omega R_p)$. Thus, in light of this and in agreement with the commenting author, the cited paper should not be considered an example of improper model employment on organic photovoltaic cells. This highlights the need for a well-defined nomenclature relating to capacitance measurements in these types of works.

It should also be noted that this does not change the general conclusions of the original work.² The cited work (Ref. 3) was merely used as jumping off point to show that improper low frequency series-mode data on P3HT:PCBM based bulk heterojenction cells could lead to misinterpretations. Although this jumping off point might now be considered ill-conceived, the data of Fig. 4 in the original article, and the conclusions drawn from it, still strongly hold. In fact, in Fig. 3 of the Comment, the author supplies series mode data for the devices presented in Ref. 3. These data are in support of that in Fig. 4 of our original article, and thereby, the general conclusions of the original article. To be clear, the general conclusion is that one must be careful in choosing the proper measurement mode when examining the capacitance of organic devices. In the simplified circuit model (Fig. 1 in Ref. 1 and Fig. 1 in Ref. 2), the parasitics are lumped into a series and shunt component (leading inductance neglected assuming frequency is low enough). Depending on the reactance $(1/(\omega C))$, either the parallel or series component may dominate and either the parallel or series mode can be used to determine the capacitance in a single measurement. Frequency is a primary factor in determining the appropriate mode. Specifically, in the high frequency limit, the reactance rapidly decreases. As it becomes comparable to R_s , the series model dominates and R_p can be neglected. In the low frequency limit, the reactance rapidly increases. As it becomes comparable to R_p, the parallel model dominates and R_s can be neglected. Between these two limits, both models are typically valid, however, one should consult ones measurement tool manual to ensure a certain model is not preferred. These limits have been qualitatively highlighted in the original article and further supported in the Comment. When considering the frequency demarcation for switching between the parallel and series model, R_s, R_p, and C must be examined. Changes in these three parameters cause a shift in the frequency demarcation. In the inorganics community, the parallel mode is indiscriminately used as it accurately models the capacitance over the frequency range of interest (from a few hertz to 1 or 2 MHz). There will still be a range when the series model dominates; however, these frequencies are typically higher than what are tested. With organic devices, however, the situation is different. When compared to inorganics, organic photovoltaic cells typically have higher series resistances, higher capacitances (owing to thinner films), and lower shunt resistances. All of which contribute to a shift of the series mode demarcation to lower frequencies-pushing it into the range of typically tested frequencies. Thus, by indiscriminately monitoring, the parallel parameters on organic devices, issues can arise, and the same can be said for indiscriminately monitoring series parameters.

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