Negative capacitance in an organic solar cell observed by displacement current measurement

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Abstract. We applied displacement current measurement (DCM) to an organic solar cell (OSC) with a structure of ITO/CuPc/C₆₀/BCP/Al in order to investigate the origin of a negative capacitance (NC). In DCM curve, an anomalous characteristic that the current in backward scan was larger than that in forward scan was observed. We found that this characteristic originates from a gradual increase of an additional current, leading to NC in DCM. The additional current can be explained by the increase of the device temperature owing to a Joule heat and thermal deactivation of the exciton. Moreover, NC value was observed to be enhanced by light irradiation due to an additional temperature increase.

1. Introduction
Organic solar cells (OSCs) have been extensively studied toward practical use [1-3] since Tang invented a planar heterojunction OSC with a high power conversion efficiency (η) of 0.95% [4]. Advanced device structures such as p-type–intrinsic–n-type layers [5, 6], bulk-heterojunction [7, 8], and tandem cell structures [9, 10] have been developed to improve η. In addition, the insertion of additional layers between the electrode and organic layer has also enhanced the device efficiency and lifetime [11, 12]. It is progressing well, however, as the device structures gradually become complex, it has become difficult to clarify the operation mechanism, resulting in incomplete design guidelines for OSCs.

The investigation about the charge carriers in OSCs is valuable in order to understand the device physics because their behaviors, such as charge injection, dissociation, recombination, and extraction processes, determine the device performance. Thus the impedance spectroscopy (IS) [13, 14], time-of-flight (TOF) [15, 16], charge extraction by linearly increasing voltage (CELIV) [15, 17], and displacement current measurements (DCM) [18] have been applied to evaluate them. Among these techniques, IS is the most widely used one and the device parameters have been analyzed based on, mainly, the frequency dependence of the capacitance of the device.

In IS measurements of organic devices, a negative capacitance (NC) is often observed at high bias and low frequency, and has been explained by various models, e.g., the recombination current [19], electron injection through interfacial states [20, 21], charge trapping [22], bias dependent conductivity modulation [23], etc. Recently, a self-heating model has been proposed by Okamoto and Tsutsui [24], and Knapp and Ruhstaller have confirmed the validity by simulation [25]. In addition, they found that NC originates from self-heating induced current enhancement. In IS, the transient response cannot be
correctly evaluated because it does not show a periodical change [26]. Although the advancement in the comprehension of NC is made, no studies have ever tried to evaluate the NC phenomenon in OSCs based on the self-heating model.

In this study, we applied DCM to a prototypical OSC with a structure of ITO/CuPc/C_{60}/BCP/Al, in order to investigate the origin of NC through the direct measurement of the flowing current. We found that NC observed in DCM originates from an anomalous characteristic that the current in the backward (positive to negative bias) scan was higher than that in the forward (negative to positive bias) scan. A transient current measurement revealed that this inversion, which does not normally occur, arises from a gradual increase in current owing to the self-heating effect of the device, leading to the NC in DCM. Finally, an impact of the light irradiation on NC is discussed based on the properties of the transient current.

2. Experimental

We prepared a OSC with a structure of ITO (50 nm)/ copper phthalocyanine (CuPc) (30 nm)/ C_{60} (40 nm)/ bathocuproine (BCP) (10 nm)/ Al (100 nm). Depositions of the organic materials and metal were done in the dark at the deposition rate of typically 1 Å/s and 3-5 Å/s, respectively, with a pressure of below 10^{-4} Pa. An active area of organic layer was 4 mm². After the deposition, the device was transferred to the glove box filled with pure N₂, and encapsulated without exposure to air.

In DCM, a triangular wave voltage (V) is applied to the sample, and the current response which is the sum of the actual current (I_{act}) and the displacement current (I_{dis}) is measured. Because I_{dis} is proportional to the effective capacitance (C) of the device as well as a ramp-rate (dV/dt) in quasi-static state (I_{dis} = C(dV/dt)), the total current in forward scan (I^+) can be expressed by

\[ I^+ = I_{act} + C \frac{dV}{dt} \]  \hspace{1cm} (1)

Similarly, the total current in backward scan (I^-) is given by

\[ I^- = I_{act} - C \frac{dV}{dt} \]  \hspace{1cm} (2)

From the difference between the equations (1) and (2), C can be obtained as

\[ C = \frac{(I^+ - I^-)}{2|dV/dt|} \]  \hspace{1cm} (3)

C normally shows a positive value since I^+ is larger than I^- because of C|dV/dt| term.

The electrical measurements were performed in the dark or under illumination with an AM 1.5 solar simulator (Asahi spectra, HAL-320) at room temperature. Note here that a cold filter was inserted between the device and a solar simulator in order to suppress the increase of the device temperature by an infrared light. For the DCM measurements, the measurement system for ferroelectrics (Toyo Corporation, FCE-1) was employed. The voltage sweep was started from the minimum voltage of the triangular wave (V_{min}) in all DCM experiments.

3. Results and discussion

3.1. DCM evaluation for organic solar cell

Figure 1 shows DCM curves in the dark at the ramp-rate of 0.1 V/s. V_{min} and the maximum voltage (V_{max}) of the triangular wave were set to be –0.5 V and 0.5 V, respectively. Solid and dotted lines indicate I^+ and I^-, respectively. The expanded figures of the regions (I), (II), and (III) are shown in the insets, clearly indicating the difference between I^+ and I^- in region (I). In region (II), C was a positive value because of I^+ > I^-.

Intriguingly, I^+ and I^- intersected at 445 mV in region (II) and finally I^- became larger than I^+ in region (III). These results imply that C which is obtained from the equation (3) varied from a positive to a negative value at 445 mV.
Figure 1. DCM curves in forward (solid line) and backward (dotted line) scans at the ramp-rate of 0.1 V/s. The insets indicate the expanded figures of the regions (I), (II), and (III).

Figure 2(a) indicates $V$ dependence of $C$ calculated from the equation (3) (CV curve), and $V_{\text{max}}$ was changed from 0.5 V to 1.5 V in 0.2 V step. The inset shows the expanded figure of DCM curve at $V_{\text{max}}$ of 0.5 V, showing that $C$ became negative at higher voltage than 445 mV. In these way, NC phenomenon of OSC was observed in DCM as well as IS measurements. In figure 2(a), at first, $C$ decreased with increasing $V$ from 445 mV and reached the minimum value of $C$ ($C_{\text{min}}$). Then $C$ increased with $V$ and finally became zero at $V_{\text{max}}$. In addition, the absolute value of $C_{\text{min}}$ ($|C_{\text{min}}|$) increased with increasing $V_{\text{max}}$. In order to directly evaluate $V_{\text{max}}$ dependence in more detail, $I^+$ and $I^−$ were separately plotted as shown in the left and right figures of the figure 2(b), respectively. $I^+$ coincided well each other, while $I^−$ increased with increasing $V_{\text{max}}$. All these things make it clear that $V_{\text{max}}$ dependence of $C_{\text{min}}$ originates from the increase of $I^−$, indeed, an additional current ($I_{\text{add}}$) which prominently appears during the backward scan and depends on $V_{\text{max}}$.

Figure 2. (a) CV curves when $V_{\text{max}}$ was changed from 0.5 V to 1.5 V in 0.2 V step. The inset indicates the CV curves at $V_{\text{max}}$ of 0.5 V. (b) $V_{\text{max}}$-dependence of DCM curves in forward (left figure) and backward (right figure) scans.

One explanation for the origin of $I_{\text{add}}$ may be a transient response of the current. Figure 3(a) shows the ramp-rate dependence of $C$ at $V_{\text{max}} = 1.5$ V, and the ramp-rate was varied from 0.1 V/s to 4 V/s. $C_{\text{min}}$ drastically increased with an increase in the ramp-rate, suggesting that $I_{\text{add}}$ strongly depends on the time.
Before turning to the discussion about the origin of NC, we must draw attention to the effect of light irradiation. Figure 3(b) shows CV curves in the dark (solid line) and under illumination (dotted line). The shape of CV curve under illumination was similar to that in the dark, while $|C_{\text{min}}|$ drastically increased by light irradiation. Thus, it is clear that $I_{\text{add}}$ is strongly affected by the light irradiation.

Finally, the features of $I_{\text{add}}$ mentioned above can be summarized as follows:

(i) $I_{\text{add}}$ prominently appears during the backward scan (figure 1),
(ii) $I_{\text{add}}$ increases with increasing $V_{\text{max}}$ (figures 2(a) and 2(b)),
(iii) $I_{\text{add}}$ decreases with increasing the ramp-rate (figure 3(a)),
(iv) $I_{\text{add}}$ is enhanced by light irradiation (figure 3(b)).

The discussion about each feature will be presented in the next section.

3.2. Origin of negative capacitance value

As discussed in the previous section, it is likely that NC originates from the increase of $I_+$, namely, $I_{\text{add}}$ over time. The details of the time dependence of the current can be easily evaluated by keeping the voltage at constant value ($V_k$) [26]. Solid line in the figure 4 indicates the time dependence of the current in the dark when the rectangular wave voltage was applied (at 0 s, the voltage was changed to $V_k = 1$ V and held as shown in the inset). The vertical axis is the normalized value ($I_t$) by the initial current ($t = 0$ s). In the dark, $I_t$ increased by $I_{\text{add}}$ with $t$. Taking this into consideration, DCM and CV curves can be explained as follows: Firstly, $I_{\text{add}}$ starts to flow from a certain voltage ($V_s$) in forward scan (figure 1), and gradually increases with $t$. Because $I_{\text{add}}$ continues to increase even in backward scan if the applied voltages are higher than $V_s$, $I_+$ becomes larger than $I_-$, resulting in the appearance of NC (feature (i)). Since $I_t$ was not saturated within 100 s (figure 4), in the case of the same ramp-rate, the higher $V_{\text{max}}$ is, the larger $I_{\text{add}}$ flows (figure 2(a)), leading to the enhancement of $|C_{\text{min}}|$ with $V_{\text{max}}$ (feature (ii)). In the same way, $C_{\text{min}}$ increased with increasing the ramp-rate (figure 3(a)) because $I_{\text{add}}$ becomes smaller by shortening of the time (feature (iii)). One can be fairly certain that the NC observed in DCM originates from $I_{\text{add}}$ which depends not directly on the applied voltage and current at which NC appears, but on the time and $V_{\text{max}}$. 

![Figure 3. (a) Ramp-rate dependence of CV curves in the dark. (b) CV curves in the dark (solid line) and under illumination (dotted line).](image-url)
In order to discuss the origin of $I_{\text{add}}$, it is important to consider the transport mechanism of charge carriers because the appearance of $I_{\text{add}}$ actually implies the variation of conductance of the device. In organic semiconductors, charges spend most of their time on localized deep states where they cannot contribute to current [27]. It must be noted that the trap states are not steadily filled with the charges, indeed, the states repeatedly trap and release the charges in the transport level [21,28]. One example of this is Poole-Frenkel conduction, which includes temperature- and field-dependent mobility [28]. Because $I_{\text{add}}$ increases even at the constant applied voltage as shown in the figure 4, it is likely that $I_{\text{add}}$ was not enhanced by the applied field, in other words, it is clear that the conductance was changed by the temperature variation of the device.

The most likely explanation for the temperature variation of the device is that the heat is generated by the flowing current (Joule heat) and a thermal deactivation of the exciton, that is, a self-heating occurs. In the framework of Poole-Frenkel conduction, the current increases with temperature because the charges can be thermally excited from the trap states into the transport level. Since the $I_n$ was not saturated within 100 s, $I$ becomes higher than $I'$ immediately after the start of the backward scan (figure 1), resulting in the appearance of $I_{\text{add}}$ (feature (i)). In like manner, $I_{\text{add}}$ increases with $V_{\text{max}}$ (figure 2(a)) because the device temperature continues to increase (feature (ii)). On contrary, $I_{\text{add}}$ decreases with increasing the ramp-rate (figure 3(a)) since there is not enough time to increase the device temperature (feature (iii)).

We are now ready to consider the effect of the light irradiation on NC value observed in DCM (feature (iv)). Although the shape of CV curve under illumination was approximately in agreement with that in the dark, $|C_{\text{min}}|$ drastically increases by light irradiation as shown in the figure 3(b). Dotted line in the figure 4 indicates the time dependence of the current under illumination when the rectangular wave voltage ($V_k = 1$ V) was applied at 0 s. The light irradiation was started a few seconds before $V_k$ became 1 V. This result shows that $I_{\text{add}}$ under illumination was much larger than that in the dark. It seems reasonable to suppose that the enhancement of $I_{\text{add}}$ by light irradiation leads to the increase of $|C_{\text{min}}|$ under illumination.

As discussed above, again, the two causes of the conductance variation are considered to be the temperature and the applied field. One can safely state that no field-assisted variation occurs because the applied voltage was fixed at 1 V. These results imply that the device temperature is increased by light irradiation, resulting in the enhancement of NC value.

4. Conclusions
In DCM, we investigated the origin of NC phenomenon of OSCs with a structure of ITO/ CuPc/ C60/ BCP/ Al. We found an anomalous characteristic that the current in backward scan is larger than that in
forward scan, leading to the appearance of NC in DCM. Transient current measurement revealed that this characteristic originates from the gradual increase of the additional current with time. This current can be explained by the increase of device temperature resulting from a self-heating effect. Moreover, the absolute value of NC observed in DCM drastically increased by the light irradiation. From the comparison of transient current in the dark and under illumination, we concluded that the device temperature was increased by the light irradiation, leading to the enhancement of NC value. Because of the low power conversion efficiency of the OSCs, the major part of the input power by light irradiation would be changed to the heat due to the thermal deactivation of the excitons. Thus we believe that the detailed analysis of NC phenomenon by DCM leads to the understanding of the charge recombination mechanism in OSCs.

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