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On the validity of MIS-CELIV for mobility determination in organic thin-film devices

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The charge extraction (of injected carriers) by linearly increasing voltage in metal-insulator-semiconductor structures, or MIS-CELIV, is based on the theory of space-charge-limited currents. In this work, the validity of MIS-CELIV for mobility determination in organic thin-film devices has been critically examined and clarified by means of drift-diffusion simulations. It is found that depending on the applied transient voltage, the mobility might be overestimated by several orders of magnitude in the case of an ohmic injecting contact. The shortcomings of the MIS-CELIV theory can be traced back to the underlying assumption of a drift-dominated transport. However, the effect of diffusion can be taken into account by introducing a correction factor. In the case of non-ohmic injecting contacts, the extracted mobility becomes strongly dependent on device parameters, possibly leading to large deviations from the actual mobility. *Published by AIP Publishing.*
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During the last decade, the charge extraction by linearly increasing voltage (CELIV) technique has become one of the most popular methods to determine the mobility in thin-film devices based on organic semiconductors, such as organic solar cells.[1,2] The main advantage of CELIV is that it can be used to simultaneously measure both the charge carrier density and mobility in operational thin-film devices.[3–7] However, in undoped (or fully depleted) devices, charge carriers have to be introduced prior to extraction which is typically achieved either by injection or photogeneration. Under these circumstances, it is in practice only possible to measure the mobility of the faster carrier.[6,8] Furthermore, the mobility evaluation has been found to be strongly sensitive to carrier profiles[7,9] and recombination rates[10] within the device. To overcome these shortcomings, the idea to use CELIV on metal-insulator-semiconductor (MIS) structures, so called MIS-CELIV, was recently developed by Juška and coworkers.[8,11] In a MIS-CELIV measurement, sometimes also referred to as i-CELIV,[12] charges are injected from the contact into the semiconductor and driven towards the insulator by an applied dc voltage. The charges are subsequently extracted at the injecting contact by a ramp up voltage pulse of reverse polarity, and the carrier mobility is determined from the extraction current transient. Depending on the polarity of the dc voltage, the hole or electron mobility can be selectively determined. However, MIS-CELIV is based on the theory of space-charge-limited (SCL) extraction current transients that assumes drift-dominated transport, neglecting the influence of diffusion. In this letter, the validity of this assumption and the impact of diffusion are clarified. It is found that not accounting for diffusion when evaluating the mobility from MIS-CELIV in organic thin-film devices might lead to errors of several orders of magnitude.

A schematic picture of the MIS-CELIV method is shown in Fig. 1. The device consists of a metal-insulator-semiconductor structure, assumed to be in contact with an injecting electrode at $x = d_s$, where the insulator-semiconductor interface is at $x = 0$; see Fig. 1(a). For a one-dimensional current flow, the total transient current response is independent of x ($\nabla \cdot \boldsymbol{j} = dj/dx = 0$) and given by[13]

$$j(t) = J_c(x,t) + \epsilon\epsilon_0 \frac{\partial E(x,t)}{\partial t}, \tag{1}$$

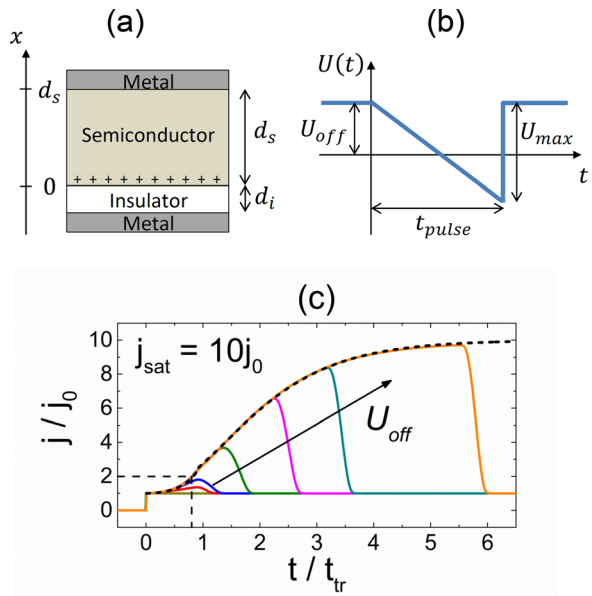

FIG. 1. A schematic of the device structure used in MIS-CELIV is depicted in (a). The MIS-CELIV voltage pulse applied over the sample is shown in (b). By applying a dc offset voltage that injects carriers (in this case, holes) from the injecting electrode (top metal) a surface charge can be accumulated at the insulator-semiconductor interface. Upon applying a reversely biased linearly increasing voltage pulse at $t = 0$, the injected surface charge can be extracted. In (c), the corresponding extraction current transients in the drift-dominated regime are shown for different offset voltages. The analytical approximation for SCL extraction current transients [Eqs. (7) and (8)] is indicated by the dotted line.

where $J_c(x,t)$ is the conduction current density, $E(x,t)$ is the electric field, and $\epsilon = \epsilon_i$ for $-d_i < x < 0$, while $\epsilon = \epsilon_s$ for $0 < x < d_s$. Here, d_s (d_i) and ϵ_s (ϵ_i) is the thickness and the dielectric permittivity of the semiconductor (insulator) layer, respectively. The insulator is assumed to be ideal and block all carriers, so that $J_c(x,t) = 0$ is always satisfied for $-d_i < x < 0$.

The device is initially assumed to be empty, corresponding to an undoped semiconductor layer. By applying a dc offset voltage U_{off} that drives carriers towards the semiconductor-insulator interface, a sheet of injected charge carriers can be created at the insulator-semiconductor interface. Upon applying an oppositely biased linearly increasing voltage pulse (with respect to U_{off}) at $t = 0$ (Fig. 1(b)), the sheet of injected carriers initially concentrated at $x = 0$ can be extracted at $x = d_s$. The corresponding extraction current transient reads[11]

$$j(t) = j_0 + \Delta j(t), \tag{2}$$

where j_0 is the current response due to the charging of the total geometric capacitance, and $\Delta j(t)$ is induced by the movement of mobile carriers within the semiconductor layer. This current is ultimately limited by the capacitance of the insulator, with the upper limit of $j(t)$ given by

$$j_{sat} = \frac{\epsilon_i \epsilon_0 A}{d_i}, \tag{3}$$

where $A = |\frac{dU}{dt}|$ is the voltage rise speed (assuming the sign of the extraction current to be positive), and $U(t)$ is the external applied voltage. In the original derivation by Juška *et al.*[11] only the limiting case when the capacitance of the insulator is much larger than the capacitance of the semiconductor layer was considered.[12] In the case of a finite insulator capacitance, however, we find (see supplementary material)

$$j_0 = \epsilon_0 A \Big/ \left(\frac{d_s}{\epsilon_s} + \frac{d_i}{\epsilon_i}\right), \tag{4}$$

$$\Delta j(t) = \frac{1}{d_s}\int_0^{d_s} \frac{J_c(x,t)}{[1+f]}\,dx, \tag{5}$$

where $f \equiv \frac{\epsilon_s d_i}{\epsilon_i d_s} = \frac{j_0}{j_{sat}-j_0}$ is the ratio between the geometric capacitance of the semiconductor and the insulator layer.

The extraction current transients (in the drift-dominated regime) are shown at different U_{off} in Fig. 1(c). At small U_{off}, when the injected charge is not large enough to perturb the electric field ($\Delta j \ll j_0$), the carriers are extracted as a uniform sheet of charge. The corresponding small-charge transit time for the sheet of carriers to reach the extracting contact is given by

$$t_{tr} = \sqrt{\frac{2d_s^2}{\mu A}(1+f)} = \sqrt{\frac{2d_s^2}{\mu A^*}}, \tag{6}$$

where $A^* \equiv A/(1+f)$. At high U_{off}, the injected sheet of charge becomes large enough to form a carrier reservoir at the insulator-semiconductor interface that screens the electric field within the semiconductor layer. In this case, the insulator-semiconductor interface will behave similarly to a reservoir-type ohmic contact, resulting in SCL extraction current transients. Assuming the transport to be drift-dominated, the SCL extraction current transient within the first time interval $0 \le t \le t_{sc}$ reads (see supplementary material)

$$j(t) = j_0\left[1 + \tan^2\left(\frac{t}{t_{tr}}\sqrt{\frac{1}{1+f}}\right)\right], \tag{7}$$

where $t_{sc} \approx 0.92 t_{tr}$ is the time at which the leading front of charge carriers arrives at the extracting contact. At larger times, $t > t_{sc}$, the current approximates to

$$j(t) = j_0 + (j_{sat} - j_0)\tanh^2\left(\frac{3t}{2t_{tr}}\sqrt{\frac{j_0}{j_{sat}}}\right). \tag{8}$$

The analytical approximations, Eqs. (7) and (8), are indicated by the dotted line in Fig. 1(c). The detailed derivation of Eqs. (7) and (8) is presented in the supplementary material.

The mobility of the injected carrier type is most conveniently estimated from the time t_1 at which the SCL extraction current transient $j(t_1) = 2j_0$. Utilizing Eqs. (6) and (7), the mobility is related to t_1 via

$$\mu = \frac{2d_s^2}{A^* t_{tr}^2} = \frac{\pi^2 d_s^2}{8A^* t_1^2}(1+f). \tag{9}$$

Here, the factor $(1+f)$ originates from taking into account the displacement current of the insulator. A necessary requirement for Eq. (9) to be valid is that $j_{sat} > j_0[1-\ln(2)]^{-1} \approx 3.3 j_0$, which ensures that $t_1 < t_{sc}$. In the limit $f \to 0$, corresponding to $j_{sat} \gg j_0$, the result by Juška *et al.*[11] is reobtained.

The MIS-CELIV theory (Eqs. (7) and (8)) fundamentally relies on the assumption that the transport within the semiconductor layer is drift-dominated. To check the validity of this assumption in organic semiconductor devices, such as organic solar cells, a numerical drift-diffusion model[14,15] is used. A hole-only device is assumed, with a semiconductor thickness of 180 nm and a hole mobility of 10^{-4} cm^2/V s. The injecting contact, in this case the anode, is assumed to be ohmic, as typically desired for diode applications. In Figs. 2(a) and 2(b), current transients at $A = 2 \times 10^4$ V/s and $A = 10^6$ V/s, respectively, are simulated for the case with $j_{sat} = 10 j_0$ ($f = 1/9$). Upon comparing the simulated MIS-CELIV current transients with the analytical SCL transients, we see that the drift-dominated SCL theory underestimates the current transients. The deviation is found to be larger at lower A. As a consequence, Eq. (9) inevitably overestimates the actual mobility, giving 2.6×10^{-3} cm^2/V s and 1.8×10^{-4} cm^2/V s for the transients in Figs. 2(a) and 2(b), respectively. Only in the limit of very large A ($\to \infty$), simulated in Fig. 1(c) (solid lines), do the extraction current transients (for large U_{off}) coincide with the analytical SCL theory (dotted lines).

The reason for the underestimation of the extraction current transients by Eqs. (7) and (8) can be traced back to the assumption of a negligible amount of background carriers within the semiconductor layer made in Eq. (7). As the accumulated carrier reservoir at the semiconductor-insulator interface mimics an ohmic contact at $x = 0$, the device will behave similar to a single-carrier device with two symmetric

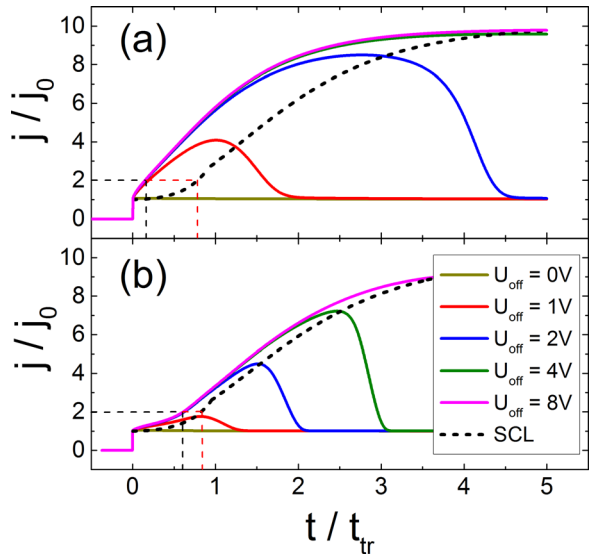

FIG. 2. Simulated MIS-CELIV current transients for (a) $A = 2\,\mathrm{V}/100\,\mu\mathrm{s}$ and (b) $A = 10\,\mathrm{V}/10\,\mu\mathrm{s}$ of an organic semiconductor device with a hole-ohmic injecting anode and an insulating layer at the cathode, assuming $j_{sat} = 10j_0$. The SCL extraction current limit, Eqs. (7) and (8), is indicated by the dotted line.

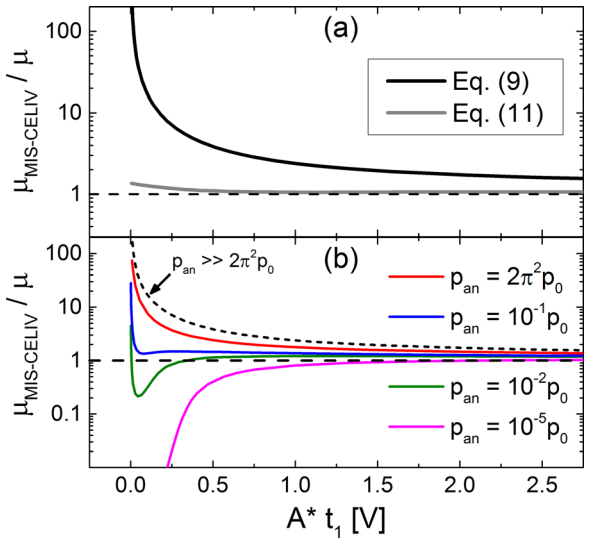

FIG. 3. MIS-CELIV mobilities $\mu_{\mathrm{MIS-CELIV}}$, normalized to the input mobility μ and extracted from the simulated current transients, as a function of A^*t_1. In (a), $\mu_{\mathrm{MIS-CELIV}}$ obtained using Eqs. (9) and (11) is shown for the case with an ohmic injecting contact ($p_{an} \gg 2\pi^2 p_0$). In (b), $\mu_{\mathrm{MIS-CELIV}}$ obtained by Eq. (9) is shown for different non-ohmic anodes. The associated hole densities p_{an} at $x = d_s$, given in units of $p_0 = \epsilon_s\epsilon_0 kT/e^2 d_s^2$, correspond to the injection barriers of 0.27 eV ($2\pi^2 p_0$), 0.41 eV ($10^{-1} \times p_0$), 0.47 eV ($10^{-2} \times p_0$), and 0.65 eV ($10^{-5} \times p_0$) at the anode in this case.

ohmic contacts. Due to diffusion, this results in a non-negligible hole density within the semiconductor layer prior to the extraction pulse (see Fig. S1 (supplementary material)). The corresponding diffusion-induced hole density in the center of the semiconductor layer (at $x = d_s/2$) is given by $p_{center} = 2\pi^2\epsilon_s\epsilon_0 kT/e^2 d_s^2$.[16,17] These carriers give rise to an additional ohmic current contribution from the semiconductor layer. The associated conduction current is given by $J_{ohm} = \frac{1}{d_s}\int_0^{d_s} J_c(x)dx = 2ep_{center}\mu V_s/d_s$,[16] where V_s is the applied voltage over the semiconductor layer.

When this diffusion-induced ohmic contribution dominates the current in Eq. (5), we expect $\Delta j(t) \approx 2ep_{center}\mu A^* t/d_s(1+f) = j_0 t/t_D$ at small extracting voltages $V_s = A^* t$, where $t_D = \frac{ed_s^2}{4\pi^2\mu kT}(1+f)$. A necessary condition for the drift-dominated SCL regime to be valid is that $t_1 \ll t_D$. In terms of A^*t_1, this condition can be re-expressed as

$$A^* t_1 \gg \frac{A^* t_1^2}{t_D} = \frac{\pi^4 kT}{2e}, \tag{10}$$

where t_1 is obtained from Eq. (9) for $t_1 \ll t_D$. If Eq. (10) is not fulfilled, Eq. (9) will inevitably overestimate the mobility in this case. In the limit $A^*t_1 \ll \frac{\pi^4 kT}{2e}$, in turn, we expect $t_1 \to t_D$, becoming independent of A^*. In this limit, t_1 is related to the mobility via $\mu \approx \frac{ed_s^2}{4\pi^2 t_1 kT}(1+f)$. Eq. (9) subsequently overestimates the mobility by $\sim \frac{\pi^4 kT}{2e}/A^* t_1$ in this case. The extracted MIS-CELIV mobility as a function of A^*t_1 is simulated in Fig. 3(a). As expected, Eq. (9) generally overestimates the mobility. Close to $A^*t_1 = \frac{\pi^4 kT}{2e} \approx 1.26$ V (at room temperature), the mobility is overestimated by a factor of two. At smaller transient voltages, the deviation becomes larger and, depending on the value of A^*t_1, the mobility might be overestimated by several orders of magnitude. The use of Eq. (9) is only justified at large A^*t_1 when drift dominates the transport.

For a general A^*t_1, the two limiting cases can be united by introducing an *ad hoc* correction factor $\left[1 + \frac{\pi^4 kT}{2e}/A^* t_1\right]$ that modifies Eq. (9) as

$$\mu = \frac{\pi^2 d_s^2 (1+f)}{8A^* t_1^2}\left[1 + \frac{\pi^4 kT}{2eA^* t_1}\right]^{-1}. \tag{11}$$

Indeed, as seen from Fig. 3(a), and excellent agreement between Eq. (11) and the numerical simulations is obtained; the relative error is below 10% over a wide range of A^*t_1. At low A^*t_1, however, a small deviation between Eq. (11) and the simulations is obtained. This deviation is caused by an additional diffusion contribution to the current (typically referred to as diffusion capacitance),[18] increasing the capacitance of the semiconductor layer in the beginning of the pulse when $A^* t \sim kT/e$. We note that the trend in Fig. 3(a) is also observed experimentally in hole-only P3HT devices (see Fig. S3 (supplementary material)), where the mobility obtained by Eq. (9) increases sharply by several orders of magnitude when A^*t is decreased below $\sim$1 V.

The above analysis is valid for ohmic injecting contacts, corresponding to the case when the hole density at the anode $p_{an} \gg p_{center}$. If, however, an injection barrier is present at the anode (under dc conditions), so that $p_{an} \ll p_{center}$, a different scenario arises. In this case, provided that a hole reservoir can still be created at $x = 0$, the device will behave as an asymmetric device with an ohmic contact at $x = 0$ and a non-ohmic contact at $x = d_s$,[16] resulting in the formation of a bias-induced built-in potential V^* within the semiconductor layer under equilibrium dc conditions (see Fig. S2 (supplementary material)). Due to the presence of V^* driving carrier towards the insulator interface, all carriers are initially concentrated at $x = 0$. Moreover, upon applying the ramp up pulse at $t = 0$, the carriers have to diffuse against the built-in

potential in order to be extracted. Concomitantly, the drift-dominated SCL extraction regime is not reached until the applied transient voltage A^*t is large enough to overcome the built-in potential, shifting the SCL extraction regime towards larger times.

The MIS-CELIV mobilities, obtained by Eq. (9), are shown in Fig. 3(b) for different non-ohmic injecting contacts. Indeed, by increasing the injection barrier (decreasing p_{an}), the overestimation of the mobility is reduced as the amount of diffusion-induced carriers within the semiconductor layer is reduced. At large injection barriers, when V^* eventually becomes significant, Eq. (9) starts to *underestimate* the mobility, leading to a deviation by several orders of magnitude at $A^*t \lesssim V^*$. In the above simulations, we assumed that the current is zero prior to the extracting voltage pulse, implying that an equilibrium is reached under dc conditions. However, if this condition is not met, for example due to an imperfect (leaking) insulator layer, V^* also becomes dependent on U_{off}.[19] Finally, it should also be noted that the apparent At_1-dependence of the mobility obtained by Eq. (9) in Fig. 3 might easily be mistaken for a field dependence if the impact of the injecting contact is not taken into account.

In conclusion, the validity of using MIS-CELIV for determining the mobility in thin-film structures has been evaluated. In the case of an ohmic contact, MIS-CELIV will overestimate the mobility, and at small transient voltages, this overestimation might be several orders of magnitude. By introducing a correction factor that takes diffusion into account, we show that this limitation can be resolved. In the case when a large injection barrier is present at the injecting contact, on the other hand, a bias-induced built-in potential will be present under dc conditions, which might result in severely underestimated mobilities.

See supplementary material for analytical derivations, additional simulations, and experimental demonstrations.

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