Carrier mobility of organic semiconductors based on current-voltage characteristics

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Carrier mobility is one of the most critical parameters in organic electronics. There is a strong interest in measuring the mobility of thin-film organic semiconductors using simple techniques, such as from current-voltage (*I-V*) measurements. This paper discusses how to extract mobility from *I-V* characteristics, ranging from space charge limited current (SCLC) to injection limited current (ILC). It is found that the mobility extracted from SCLC may significantly deviate from the value measured by time-of-flight depending on the contacting nature at the injection interface. Therefore, the SCLC cannot in general be used to accurately measure mobility. However, the mobility extracted from ILC, which incorporates the injection barrier height measured by ultraviolet photoelectron spectroscopy, is found to be more reliable for unknown materials systems. © *2010 American Institute of Physics*. [doi:10.1063/1.3305341]

I. INTRODUCTION

Semiconducting small molecules and conjugated polymers are of broad interest for next generation optoelectronic device applications, such as organic light emitting diodes (OLEDs)[1–3] and organic photovoltaics (OPVs).[4,5] Among the design criteria for new organic semiconducting materials, carrier mobility is by far one of the most important parameters to many aspects of device design and performance. For example, it is well recognized that a balanced hole and electron mobility are necessary to achieve high efficacy in OLEDs and high fill factors in OPVs. Also, the low mobility of current organic materials limits the overall device performance, which in many cases is less than optimal. As a result new materials with higher mobility are highly sought after. Carrier mobility measurements are therefore common practice in the screening of new materials for device applications.

Of the commonly used techniques to measure mobility, time-of-flight (TOF) is by far the most accurate method. However, TOF is often not practical for evaluating the mobility of new materials since it requires several micron thick films and specialized equipment. What is more, it is often difficult to replicate the morphology of the thin films used in devices (typically ~100 nm) in the micron thick films required for TOF measurements. As a result, simplified measurement techniques such as the so called space charge limited current (SCLC) method have become extremely popular.[6–12] The SCLC method is advantageous since it requires significantly thinner sample thicknesses as well as simpler experimental apparatus. For example, it only requires a commonly available source measurement unit to extract the mobility from a simple diode structure (e.g., anode/organic/cathode). However, care must be taken when applying this technique since it requires a strict condition of

an Ohmic contact at one of the electrode/organic interfaces (i.e., at either the anode or cathode). However, if the injection barrier at the electrode/organic interfaces are unknown (as is typical with most materials), direct application of the SCLC method often results in physically meaningless analysis. Although the SCLC technique has been used since the 1950s[13] and has been thoroughly discussed in many textbooks,[14,15] the frequency of misuse in literature warrants an up-to-date discussion of common pitfalls, especially for the case of organic semiconductors.

In this paper, we discuss the application of the SCLC method to estimate the mobility of organic semiconductors and provide several experimental examples of common pitfalls. Methods of avoiding these pitfalls are also discussed along with an example using the measured barrier height from ultraviolet photoelectron spectroscopy (UPS) measurements. This work sheds new light on some of the recently reported discrepancies in device performance for newly synthesized organic materials.

II. EXPERIMENTAL

In this study, single carrier hole-only devices were used to evaluate the injection properties. The structure of the devices is anode/organic/cathode. N,N′-diphenyl-N,N′-bis-(1-naphthyl)-1-1′-biphenyl-4,4′-diamine (α-NPD) and 4,4′,4″-tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine (*m*-MTDATA) were used as the organic semiconductor layer. Au was used as cathode to block electron injection due to its high work function, such that the device is hole dominant.[16] Indium tin oxide (ITO), sputter deposited Al_2O_3 on Au (i.e., Au/Al_2O_3),[17] and oxidized Ni (i.e., NiO_x) were used as anode. The ITO is commercially patterned and coated on glass (50×50 mm^2) with a sheet resistance less than 15 $\Omega/\square$ and the Au/Al_2O_3 and NiO_x were fabricated on Corning® 1737 glass substrate. Substrates were ultrasonically cleaned with a standard regiment of Alconox®, acetone, and methanol followed by ultraviolet (UV) ozone treatment

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for 15 min. All devices were fabricated in a Kurt J. Lesker LUMINOS® cluster tool with a base pressure of $\sim 10^{-8}$ Torr. Devices were defined by the intersection of the top cathodes and the bottom anodes. The active area for all devices was 2 mm². The film thicknesses were monitored by a calibrated quartz crystal microbalance and were further verified for each sample by using both a stylus profilometer (KLA Tencor P-16+) and capacitance-frequency (*C-F*) measurements. After the deposition, samples were taken from the cluster tool and loaded into a vacuum cryostat with a base pressure of $\sim 10^{-6}$ Torr for measuring. *I-V* and *C-F* characteristics were measured using a HP4140B picoammeter and Agilent 4294A, respectively. UPS measurements were performed using a PHI 5500 MultiTechnique system, with attached organic deposition chamber with a base pressure of $\sim 10^{-10}$ Torr. More details of the device fabrication, characterization, and UPS measurements have been discussed elsewhere.[16,18,19]

III. THEORY

Before we begin the discussion of mobility measurements, we must first review the basic concepts of charge injection and transport in organic semiconductors (both small molecule and polymer). For unipolar transport (i.e., single carrier devices) the maximum charge that an organic semiconductor can achieve, i.e., when the current is SCLC, the current density follows the Mott–Gurney law,[14]

$$J = \frac{9}{8}\varepsilon_0 \varepsilon \mu \frac{V^2}{d^3}, \tag{1}$$

where V is the applied voltage and d is the thickness of the film, μ is the mobility, ε_0 is the permittivity of free space, and ε is the dielectric constant. However, the Mott–Gurney law assumes a perfect insulator with an electric field *independent mobility* (i.e., μ is a constant), which is not the case for most organic semiconductors. By using the Poole–Frenkel like field dependence of the mobility,

$$\mu(F) = \mu_0 \exp(\beta\sqrt{F}), \tag{2}$$

where F is the electric field strength, an approximation of the SCLC is given by Ref. 20 as

$$J_{SCLC} = \frac{9}{8}\varepsilon \varepsilon_0 \mu_0 \exp\left(0.89\beta\sqrt{\frac{V}{d}}\right)\frac{V^2}{d^3}. \tag{3}$$

If the electrode contact is capable of injecting sufficient charge to sustain the SCLC given by Eq. (3) then the contact is referred to as "Ohmic." Alternatively, if an energy barrier exists at the electrode contact—analogous to a Schottky contact at a metal/semiconductor interface—the current density is limited by the injection of charge rather than the bulk properties of the organic. In such a case the current density follows the so called injection limited current (ILC), which can be described by various models. Fowler–Nordheim (FN) tunneling[21] is commonly used to describe injection for inorganic semiconductors. However, it is only applicable at extremely high electric field (beyond the range for device application),[22] such that it is not suitable to use FN tunneling here to describe the injection at electrode/organic

interfaces.[23] Another commonly used injection model for the ILC in organic semiconductors has been proposed by Scott and Malliaras based on the original solution to the drift diffusion equation for injection into a wide band gap intrinsic semiconductor solved by Emtage and O'Dwyer. This model determines the equilibrium contributions to the current density for charge carriers recombining with their own image in analogy with Langevin recombination of an electron-hole pair in the bulk,[24]

$$J_{ILC} = 4N_0\psi^2 e\mu F \exp(-e\phi_B/k_BT)\exp(f^{1/2}), \tag{4}$$

where F is the applied electric field, μ is the field dependent carrier mobility, N_0 is the density of states in the organic film, ϕ_B is the barrier height, k_B is the Boltzmann constant, e is the electron charge, T is the temperature, and ψ is a function of reduced electric field $f = e^3 F/4\pi\varepsilon k_B^2 T^2$, namely,

$$\psi = f^{-1} + f^{-1/2} - f^{-1}(1 + 2f^{1/2})^{1/2}. \tag{5}$$

Notice that the ILC for organic semiconductors given by Eq. (4) also depends on the carrier mobility μ, which suggests that mobility can also be extracted by measuring the ILC if the barrier height is known (discussed below).

IV. RESULTS AND DISCUSSION

Now that we have reviewed the basic concepts of charge injection and transport in organic semiconductors we can move on to mobility measurements. One of the commonly used methods to measure mobility is to fabricate single carrier devices (see Ref. 16 for a review of how to properly design single carrier devices) and measure the *I-V* characteristics. Then by using the field-dependent form of the Mott–Gurney law given by Eq. (3) one can easily fit the *I-V* curve to extract the mobility from the SCLC region of the curve. This method is based on the assumption that the injection contact is Ohmic; remember Eq. (3) only describes the SCLC, which is the upper limit. However, such analysis is problematic since the Mott–Gurney law is only a necessary condition for SCLC but is not sufficient. In other words, just because a *I-V* curve can be fit using Eq. (3) does not guarantee that the contact is Ohmic; if the contact is in fact not Ohmic then the extracted mobility is physically meaningless.

To demonstrate the concept that the *I-V* characteristics alone cannot provide enough information to extract mobility, we fabricated single carrier device of α-NPD and *m*-MTDATA with Au/Al₂O₃ as anode. The current density of these two devices as a function of average electric field (i.e., $F = V/d$) is shown in Fig. 1. Imagine that these are two unknown new materials and whose mobility needs to be estimated in the first place, i.e., without any *a priori* knowledge of the contact (energy alignment) or mobility. Based on the *I-V* characteristics shown in Fig. 1, it can be easily concluded that the injection barrier height and mobility of α-NPD and *m*-MTDATA are similar, since the *I-V* characteristics are nearly identical.

However, both α-NPD and *m*-MTDATA are commonly studied hole transporting small molecules in OLEDs, and hence their properties such as mobility are well known. The mobility of α-NPD is in fact one order of magnitude larger
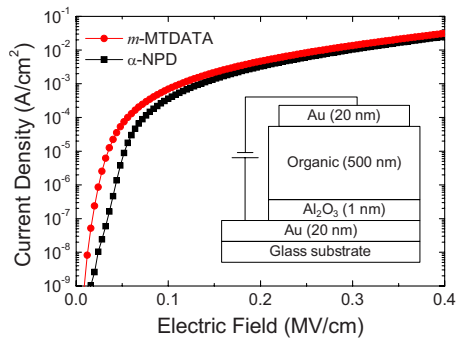
FIG. 1. (Color online) Current density as a function of average electric field (i.e., $F=V/d$) for single carrier devices with Au/Al_2O_3 anode.
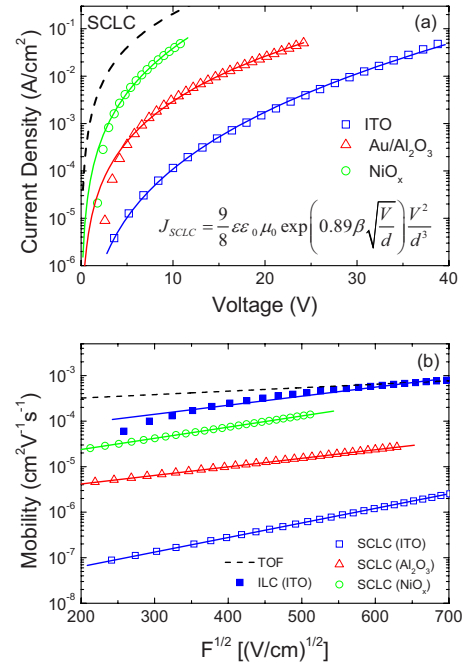

FIG. 2. (Color online) (a) Current density of α-NPD single carrier devices as a function of voltage with different anodes. The corresponding solid lines are fits using Eq. (3). The dashed line is the SCLC upper limit calculated using Eq. (3) from the TOF mobility we have reported elsewhere (Ref. 26). (b) Mobility of α-NPD extracted from SCLC with ITO, Au/Al_2O_3 and NiO_x anodes, ILC with ITO anode, and TOF.

than *m*-MTDATA,[25] despite similar *I-V* characteristics. It is noted that any possible error caused by using different sources of molecule has also been eliminated; the mobility of the same batch of molecules was measured by TOF by our group and reported elsewhere,[26] confirming that the mobility of α-NPD is indeed one order of magnitude larger than that of *m*-MTDATA. For the Au/Al_2O_3 anode the current density of *m*-MTDATA is higher than α-NPD due to the different energy-level alignment at the metal/organic interface. The injection barrier for *m*-MTDATA is much smaller than for α-NPD;[17] hence, the higher current density despite lower mobility. Discussion of the difference in energy-level alignment is beyond the scope of this work and has been discussed elsewhere.[17]

The simple example shown above demonstrates that the magnitude of current density on its own does not give enough information to accurately estimate mobility. In the following, it will be shown that we cannot determine whether the current density is SCLC by the shape (slope) of the *I-V* curve, nor can we extract the mobility by fitting the *I-V* characteristics with Eq. (3). In other words, the mobility of organic semiconductors cannot be extracted using the SCLC method without *a priori* knowledge that the injection contact is already Ohmic. To demonstrate this point Fig. 2(a) shows an experimental example of the *I-V* characteristics of α-NPD hole-only devices with ITO, Au/Al_2O_3, and NiO_x as anode. Once again the reason for choosing α-NPD is because the mobility is already well known. The dashed line in the figure shows the SCLC for α-NPD calculated using Eq. (3) from the TOF mobility we have reported elsewhere.[26] The solid lines in Fig. 2(a) are the corresponding fit to the experimental results using Eq. (3). Clearly, the calculations are all in "excellent" agreement with the experimental results. The mobility can then be extracted taking $\varepsilon=3$ (Ref. 26) and knowing the thickness of organic layer d (for example the thickness with ITO anode is 420 nm); the extracted mobility is summarized in Fig. 2(b) (hollow symbols). The extracted mobility from the device with ITO anode is almost four orders of magnitude lower than the value measured by TOF [see Fig. 2(b)], which should not be surprising given that the *I-V* curve is far from the SCLC upper limit [see Fig. 2(a)]. The other two values (extracted from Au/Al_2O_3 and NiO_x) are higher but still much smaller than the SCLC upper limit. Remember that the organic material is the same; therefore,

the extracted mobility should also be the same (regardless of how good the fit is).

The significant discrepancy between the mobility measured using the SCLC method and TOF is due to the improper assumption that the injection contact is already Ohmic. Although these anodes have a high work function (ITO $\sim$ 4.9 eV, Au/Al_2O_3 $\sim$ 5.1 eV, and Ni_2O_x $\sim$ 5.2 eV), this does not guarantee an Ohmic contact for holes, or even good hole injection. The energy-level alignment (e.g., interfacial dipole effect) has to also be considered (which was studied by the UPS measurements shown below). As a result, transport parameters, such as mobility, extracted from merely fitting the *I-V* characteristics using the SCLC method are physically meaningless without *a priori* knowledge that the injection contact is Ohmic. Moreover, the *I-V* characteristics are insufficient to determine whether the current density is SCLC (Ohmic contact) without knowledge of either mobility or injection barrier [as was demonstrated by Fig. 2(a)]. To extract mobility (injection barrier) from *I-V* characteristics, one has to first know the injection barrier (mobility).

As we have already demonstrated, direct application of the SCLC method to measure mobility can often lead to fortuitous results. How then can we accurately measure mobility without resorting to TOF? As discussed above, the ILC of organic semiconductors also depends on mobility [see Eq. (4)]. Since it is far easier to fabricate injection limited contacts than Ohmic contacts, fitting experimental ILC data should be much more reliable than the SCLC method. Obviously, this technique requires knowledge of the injection barrier, which can be accurately measured using a variety of techniques.[15] Here we elected to use UPS to measure the
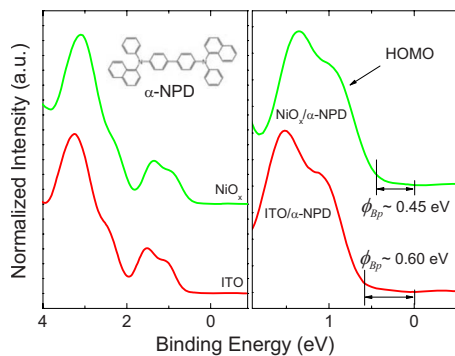
FIG. 3. (Color online) He Iα($h\nu$ = 21.22 eV) valence band spectra for 3 nm thick α-NPD deposited on NiO$_x$ and ITO. We confirmed no differential charging of the α-NPD layer by comparing the C 1s core-level binding energies at various photocurrents and sample biases.

injection barrier since it is a readily available and reliable technique. Figure 3 shows the UPS He Iα($h\nu$ = 21.22 eV) valence band spectra of α-NPD deposited on ITO and NiO$_x$ [electrodes with the smallest and largest current densities shown in Fig. 2(a)]. The injection barrier was taken as the distance (in energy) from the onset of the highest occupied molecular orbitals (HOMO) derived peak to the Fermi level at zero binding energy. The measured barrier heights are 0.60 and 0.45 eV for ITO and NiO$_x$, respectively; measurements were consistent across several different samples. We have to note that the injection barrier between ITO and α-NPD may vary due to different sources of ITO and different ITO surface treatments; however, all the results shown above are self-consistent as the same ITO and sample preparation was used throughout.

The difference between the measured injection barrier for ITO and NiO$_x$ also explains why the current density of the ITO anode is much smaller than that of NiO$_x$. As a result, the current density is determined by both the injection (interface property) and the mobility (bulk property of organic semiconductor). To describe the current density, one has to combine these two effects, for example, by using time domain simulation to calculate the transient current, which has been discussed elsewhere in greater detail.[27]

Since the injection barrier of ITO/α-NPD is very large (i.e., 0.6 eV), we can make the reasonable assumption that the current density is already ILC,[27] and hence the mobility can be estimated from the *I-V* characteristics (using the measured value of barrier height) using Eq. (4). The extracted mobility using this technique is also shown in Fig. 2(b) (solid squares). We can see that the extracted mobility is much closer to the value obtained from TOF. We have to note that this kind of analysis could also be incorrect without the *a priori* knowledge that the current density is ILC. We can easily identify that the current density is already ILC by studying the thickness dependence of the organic layer (i.e., for ILC $V \propto d$ at a fixed current density[28]). However, since the injection at the ITO/α-NPD interface with a barrier of 0.6 eV has already been shown to be ILC,[27,29] the extracted mobility using Eq. (4) should be reliable.

V. SUMMARY

In summary, we have demonstrated that it is incorrect to measure the mobility of organic semiconductors by directly applying the SCLC method without *a priori* knowledge that the injection contact is in fact Ohmic. It is found that the extracted mobility by such inappropriate methods may be orders of magnitude smaller than the value measured using TOF. Including the barrier height measured by UPS, a more accurate estimation of mobility from ILC was shown. Therefore the injection barrier height must be known if mobility is to be extracted from *I-V* characteristics.

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