Supplementary Material for ***Exploring the Validity and Limitations of the Mott-Gurney Law for Charge-Carrier Mobility Determination of Semiconducting Thin-Films***

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Supplementary information containing discussion of using Boltzmann statistics at degeneracy, additional calculation results, and the analytical derivation of the saturation current (eq. 8). These results are not essential for understanding the content of the paper, but are presented here for additional clarification if needed.

1. Boltzmann statistics at degeneracy

When the difference between the Fermi level and conduction band edge is zero, the semiconductor is said to be degenerate, so in the case of an Ohmic contact ($\phi_{\mathrm{inj}} = 0$), and $n_{\mathrm{int}} = N_{\mathrm{C}}$. Degeneracy can occur either through heavy doping or through injection of charge carriers, as in the case at the metal-semiconductor interface. Similarly, when charges are injected into the semiconductor from the injection contact, the Fermi level will approach the conduction band well beyond the 0.1 eV limit. In the limit of degeneracy, Boltzmann statistics are no longer valid to describe the carrier concentrations, and one is forced to use the exact description using Fermi-Dirac statistics,

$$n = 2N_{\mathrm{C}}\pi^{-1/2}\int_{E_{\mathrm{C}}}^{\infty}\frac{E^{\frac{1}{2}}}{(k_{\mathrm{B}}T)^{3/2}}\frac{1}{\mathrm{e}^{(E-E_{\mathrm{F}})/k_{\mathrm{B}}T}+1}\mathrm{d}E \qquad \text{(S1)}$$

The calculations performed by ASA are however performed using Boltzmann statistics, so it is inevitable to introduce a minor error when defining the Ohmic contacts as we do in this paper. However, by comparing the exact theory with the Boltzmann approximation, the error introduced is minute.

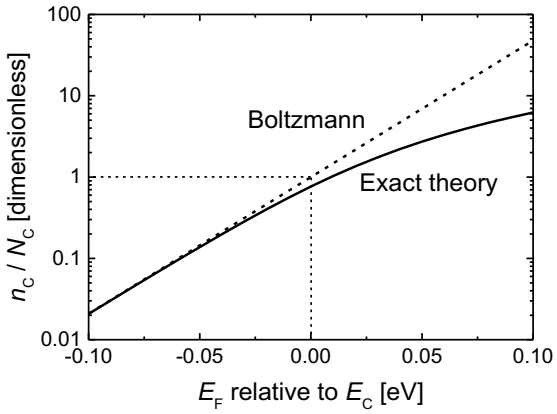

Figure S1 - Normalized charge carrier concentration calculated from the exact theory and in the Boltzmann approximation. From the exact theory, it is seen that when the Fermi level and conduction band coincides, $n = 0.77N_{\mathrm{C}}$.

From figure S1 it can be seen that the carrier concentration will be roughly $0.77 \cdot N_{\mathrm{C}}$ at the point of degeneracy ($E_{\mathrm{C}} - E_{\mathrm{F}} = 0$) for the exact theory and $n = N_{\mathrm{C}}$ for the Boltzmann approximation. It is not until the semiconductor is doped or optically excited beyond degeneracy that the Boltzmann approximation deviates dramatically from the exact theory. Since the effective mass of most organic semiconductors is not known/defined exactly (as the effective density of states is defined through the effective mass, which in turn is defined from the curvature of the band structure, something which we

don't consider for organics), little information is lost using this approximation. It should however here be noted that the onsets of the critical voltages might differ slightly due to the small variations in the carrier concentrations. The error due to using Boltzmann statistics at degeneracy is estimated to be less than 25%.

2. Derivation of eq. 8

The one dimensional drift-diffusion equation for positively charged carriers (holes) is given by,

$$\frac{J_p}{q} = -D_p \frac{dp}{dx} + p\mu_p F \qquad \text{(S1)}$$

where J_p is the current density, q is the elementary charge, D_p is the diffusion coefficient, p is the hole density, μ_p is the hole mobility and F is the electric field (holes were considered due to simplicity). By rewriting the equation on the form of a first-order differential equation in terms of the charge carrier mobility and the valence band edge we obtain,

$$\frac{dp(x)}{dx} - p(x)\frac{1}{k_B T}\frac{dE_V(x)}{dx} = -\frac{J_p}{\mu_p k_B T}. \qquad \text{(S2)}$$

We can multiply both sides of eq. S2 with the integration factor, which is given by $e^{-\frac{1}{k_B T}\int \frac{dE_V(x)}{dx}dx}$. We then obtain,

$$\left(\frac{dp(x)}{dx} - p(x)\frac{1}{k_B T}\frac{dE_V(x)}{dx}\right) e^{-\frac{1}{k_B T}\int \frac{dE_V(x)}{dx}dx} = \left(-\frac{J_p}{\mu_p k_B T}\right) e^{-\frac{1}{k_B T}\int \frac{dE_V(x)}{dx}dx}. \qquad \text{(S3)}$$

The left hand side of eq. S3 can be rewritten through the reverse product rule to be,

$$\frac{d}{dx} p(x) e^{-\frac{1}{k_B T}\int \frac{dE_V(x)}{dx}dx} = \left(-\frac{J_p}{\mu_p k_B T}\right) e^{-\frac{1}{k_B T}\int \frac{dE_V(x)}{dx}dx} \qquad \text{(S4)}$$

and by integration of both sides over the whole space-charge region (0 to L), and by using the corollary theorem of calculus, we obtain,

$$-\mu_p k_B T p(x) e^{-\frac{1}{k_B T}\int_0^L \frac{dE_V(x)}{dx}dx}\Big|_0^L = J_p \int_0^L e^{-\frac{1}{k_B T}\int_0^L \frac{dE_V(x)}{dx}dx}\, dx. \qquad \text{(S5)}$$

At high voltages, the valence band edge will depend linearly on the spatial position inside the semiconductor, and is given by,

$$E_{\mathrm{V}} = -q\left\{V + \phi_{\mathrm{inj}}\left(1 - \frac{x}{L}\right) + (\phi_{\mathrm{ext}} - V)\frac{x}{L}\right\} \qquad \text{(S6)}$$

which yield the boundary conditions for the valence band edge,

$$E_{\mathrm{V}}(0) = -q(V + \phi_{\mathrm{inj}}), \qquad \text{(S7)}$$

$$E_{\mathrm{V}}(L) = -q\phi_{\mathrm{ext}}. \qquad \text{(S8)}$$

The boundary conditions for the charge carrier density is given by the injection barrier heights and the effective density of states (assuming Boltzmann statistics),

$$p(0) = N_V \exp\left(-\frac{q\phi_{\mathrm{inj}}}{k_{\mathrm{B}}T}\right) \qquad \text{(S9)}$$

$$p(L) = N_V \exp\left(-\frac{q\phi_{\mathrm{ext}}}{k_{\mathrm{B}}T}\right) \qquad \text{(S10)}$$

The left hand side of eq. S5 can now be evaluated by using the boundary conditions for the conduction band edge (eq. S7 & S8) and the boundary conditions for the charge-carrier density (eq. S9 & S10), whereas the right hand side of the eq. S5 must be evaluated using eq. S6 (note that the integrals inside the exponentials can be evaluated using the corollary. i.e., simply from considering the boundary conditions). This evaluation leads to,

$$J_p = \frac{q\mu_{\mathrm{h}}N_{\mathrm{V}}(\phi_{\mathrm{ext}} - \phi_{\mathrm{inj}} - V)\left\{\exp\left(\frac{qV}{k_{\mathrm{B}}T}\right) - 1\right\}}{L\exp\left(\frac{q\phi_{\mathrm{inj}}}{k_{\mathrm{B}}T}\right)\left\{\exp\left(\frac{q\phi_{\mathrm{ext}} - q\phi_{\mathrm{inj}}}{k_{\mathrm{B}}T}\right) - \exp\left(\frac{qV}{k_{\mathrm{B}}T}\right)\right\}} \qquad \text{(S12)}$$

which is the general expression for the trap-free drift-diffusion hole current density in a single-carrier device neglecting band bending at the interface (flat band picture) where $\phi_{\mathrm{ext}} - \phi_{\mathrm{inj}} = V_{\mathrm{bi}}$. With $\phi_{\mathrm{inj}} = \phi_{\mathrm{ext}} = 0$ the general expression reduces to,

$$J = q\mu_{\mathrm{h}}N_{\mathrm{V}}\frac{V}{L} \qquad \text{(S13)}$$

which is Ohm's law in the saturation limit. When the injection barrier heights are non-zero and of similar height $\phi_{\mathrm{inj}} = \phi_{\mathrm{ext}} > 0$, the general expression reduces to,

$$J = q\mu_{\mathrm{h}}N_{\mathrm{V}}\frac{V}{L}\exp\left(-\frac{q\phi_{\mathrm{inj/ext}}}{k_{\mathrm{B}}T}\right) \qquad \text{(S14)}$$

which is Ohm's law in the saturation regime corrected by the injection barriers (eq. 8). Eq. S14 is only truly valid when $\phi_{\mathrm{inj/ext}} > 2k_{\mathrm{B}}T$, and close to degeneracy S13 must be corrected by a term allowing for Fermi-Dirac statistics. By combining S1 with S13, and by noting that $E_{\mathrm{F}} = E_{\mathrm{V}}$ at saturation, we can now write,

$$J = q\mu_{\mathrm{h}}\frac{V}{L}2N_{\mathrm{V}}\pi^{-1/2}\int_{-\infty}^{E_{\mathrm{V}}}\frac{E^{\frac{1}{2}}}{(k_{\mathrm{B}}T)^{3/2}}\left(1-\frac{1}{\mathrm{e}^{(E-E_{\mathrm{V}})/k_{\mathrm{B}}T}+1}\right)\mathrm{d}E \qquad \text{(S15)}$$

However, S15 cannot be evaluated analytically, but differs from S14 by around 23.5% at degeneracy and 11.5% at $k_{\mathrm{B}}T$, meaning that S14 is still a good approximation close to degeneracy.

3. Additional numerical calculations

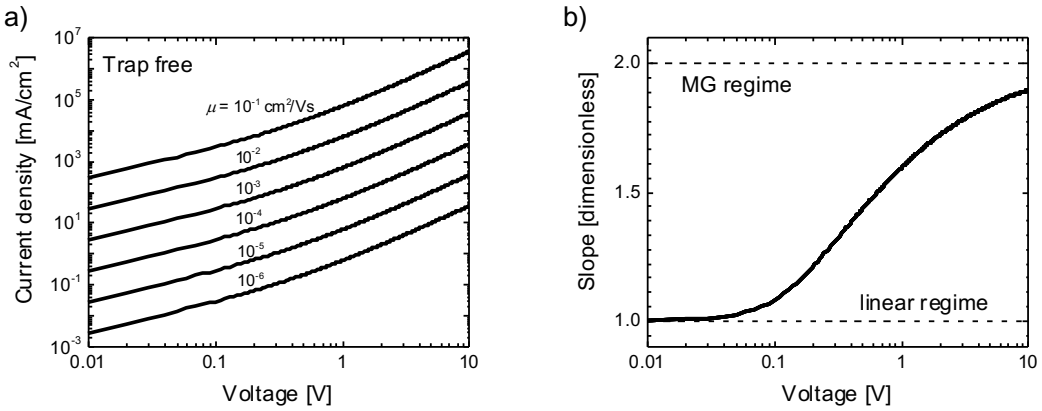

Figure S2 – The effect of the choice of mobility on the simulation results: a) *J-V* curves for trap free devices with Ohmic contacts with a varying mobility, and b) the corresponding *m-V* curves showing a complete overlap between irrespective of the choice of mobility.

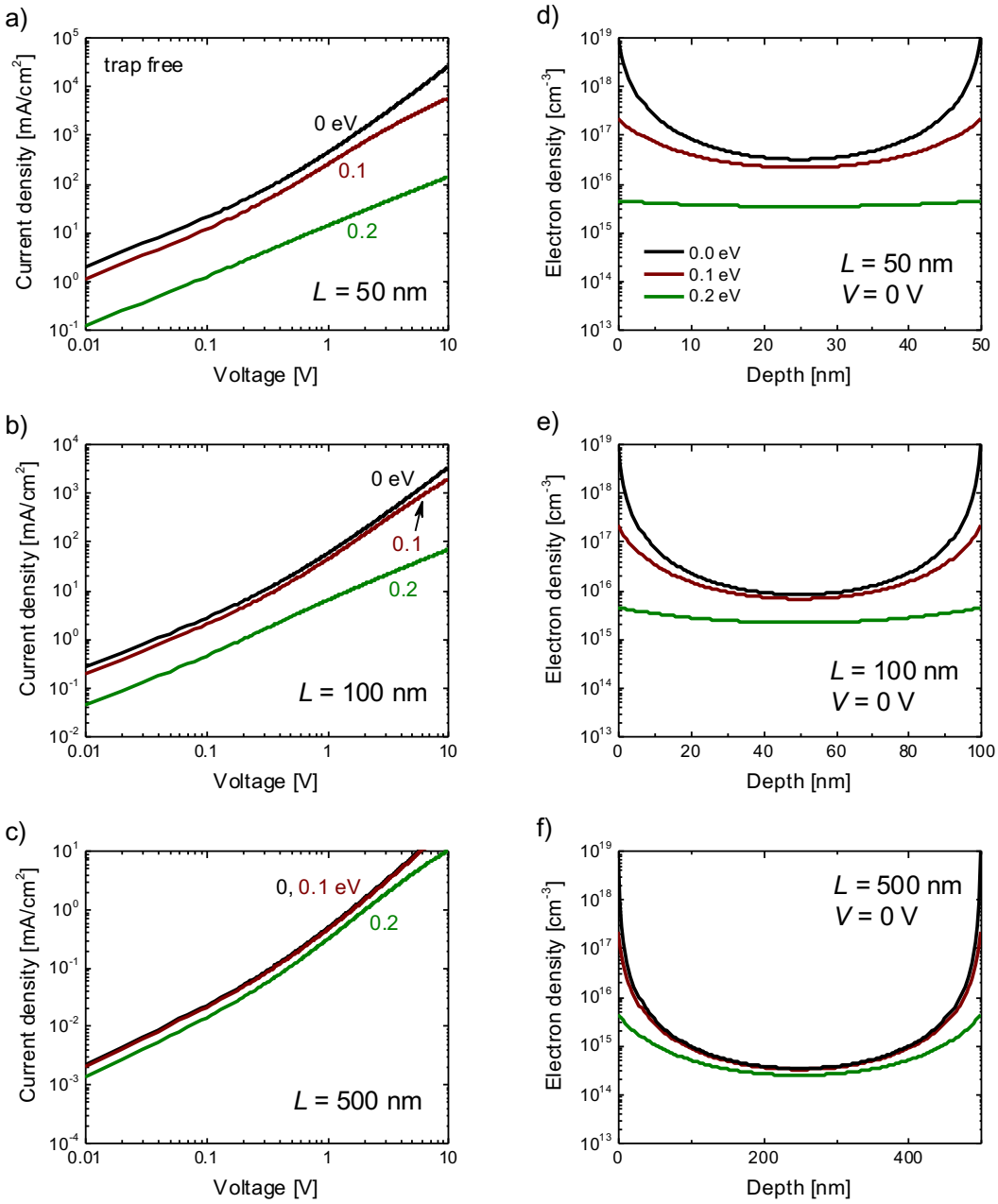

Figure S3 – Simulated *J-V* curves of single-carrier devices with varying degree of injection limitation (0, 0.026, 0.052, 0.1 and 0.2 eV): a) 50 nm, b) 100 nm and c) 500 nm. The 50 nm device not only shows a high degree of reduction in the magnitude of the current, but the transport regimes (identified by the $\boldsymbol{J \propto V^m}$ dependence) changes are highly affected at a low applied voltage. d), e) and f) shows the corresponding electron densities at 0 V.

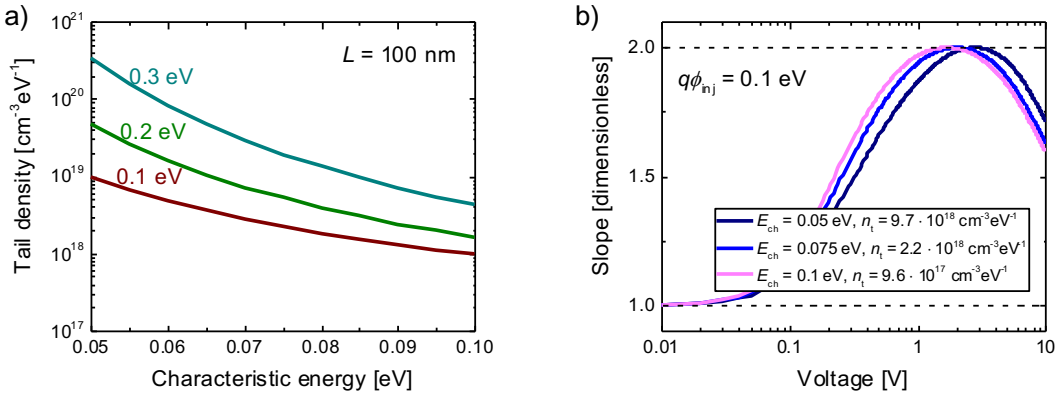

Figure S4 - a) Required tail density values at specific characteristic energies to reach $m = 2$. b) Examples of m-V curves.