Trap-controlled hole transport in small molecule organic semiconductors

Arne Fleissner,a) Hanna Schmid, Christian Melzer, and Heinz von Seggern
Electronic Materials Department, Institute of Materials Science, Darmstadt University of Technology, 64287 Darmstadt, Germany

(Received 22 June 2007; accepted 12 November 2007; published online 11 December 2007)

The influence of trap concentration on hole transport is investigated by an optical time-of-flight method for the amorphous small molecule organic semiconductor N,N’-bis(1-naphthyl)-N,N’-diphenyl-(1,1’-biphenyl)-4,4’-diamin (α-NPD) doped with neutral hole traps by codeposition of 4,4’,4”-tris[N-(1-naphthyl)-N-(phenylamino)]triphenylamine (1-NaphDATA). α-NPD doped with 120 ppm 1-NaphDATA exhibits nondispersive hole transport like undoped α-NPD, but trap-controlled with reduced mobility. The trap depth derived from the mobility decrease coincides with the ionization potential difference of α-NPD and 1-NaphDATA. The transition to dispersive transport for increasing trap concentration to 1160 ppm is explained by an energetic relaxation of optically generated charge carriers within a density of states broadened by traps. © 2007 American Institute of Physics. [DOI: 10.1063/1.2820448]

Charge carrier transport through organic semiconductors is strongly affected by trap states in the energy gap.1 Such states can be deliberately introduced by neutral doping with organic molecules which have an energy level within the energy gap of the host material.2 Such trap-induced decrease of the charge carrier mobility has been utilized to balance charge transport in organic light emitting diodes (OLEDs), resulting in an improved lifetime.3 The effect of trap concentration on charge transport has been studied in organic single crystals4 and in amorphous solid solutions of small organic molecules in polymeric binders5,6.

The present work is aimed at technologically important amorphous films consisting solely of small molecules, which can be prepared by thermal evaporation and thus exclude any effect of a polymeric binder. The influence of trap concentration on charge carrier transport type and mobility is studied by an optical time-of-flight method for hole transport through the doped solid of N,N’-bis(1-naphthyl)-N,N’-diphenyl-(1,1’-biphenyl)-4,4’-diamin (α-NPD), 4, 4’, 4”-tris[N-(1-naphthyl)-N-(phenylamino)]triphenylamine (1-NaphDATA) is used as neutral molecular dopant, which is known to create hole traps in α-NPD due to the difference of the ionization potentials.7 This renders α-NPD doped with 1-NaphDATA a good model system for investigating the effect of hole traps on hole charge transport.8

Few microns of the organic semiconductors are deposited by thermal coevaporation at a base pressure of 10−6 mbar onto a 10-nm-thick semitransparent Al electrode on a glass substrate and are topped with a thick Al counter electrode. The time-of-flight measurements9 are carried out utilizing a frequency-tripled Nd:YAG (yttrium aluminum garnet) laser (Solar Systems LQ129/LQ103) at a wavelength of 355 nm and a pulse length of 10 ns, which is used to excite an electrode-near regime of the organic layer through the semitransparent Al electrode. The transient current signal results from the motion of generated charge carriers under an applied voltage and is measured by means of a current-voltage amplifier (Femto DHPCA-100) and a digital oscilloscope (Tektronix TDS 5052). A few hundred consecutive current transients are averaged in order to decrease the noise. In all cases, a positive voltage V was applied to the semitransparent electrode, resulting in hole currents only. All experiments were performed at room temperature in inert nitrogen atmosphere. High laser light intensities were utilized to work under space-charge limited conditions, which were preferred since they allow an unambiguous determination of the charge carrier transit time even for doped systems with small charge carrier mobilities and related small transient currents. In this case, the optically generated excess charge extracted from the excited regime is in the order of CV, where C is the sample capacitance.

Current transients for undoped α-NPD and α-NPD doped with 120 ppm 1-NaphDATA are shown in Fig. 1. 120 ppm 1-NaphDATA corresponds to a trap concentration of 1.2 × 1017 cm−3 for a total density of states of approximately 1021 cm−3 for the host material. All current transients exhibit the characteristic maximum, most clearly seen in the inset of Fig. 1, which is characteristic for the space-charge regime in nondispersive transport.10 In this transport mode, the charge carriers quickly establish local thermal equilibrium and the maximum indicates the space-charge transit time τ∗, which high is related to the small signal transit time τ, describing the transit of a moving package of charge car-

FIG. 1. Hole current transients for undoped α-NPD and α-NPD doped with 120 ppm 1-NaphDATA for various applied voltages in a double logarithmic plot. The inset exemplarily shows one transient in linear scale.

a)Electronic mail: fleissner@e-mat.tu-darmstadt.de.
The field dependence of charge carrier mobility at a constant temperature can than be given as

\[ \mu = \mu^* \exp(\gamma/E), \]

with a zero field mobility \( \mu^* \) and a material constant \( \gamma \). A fit of the experimental data for undoped \( \alpha \)-NPD yields \( \mu^* \approx 4.8 \times 10^{-3} \text{ cm}^2/\text{Vs} \) and \( \gamma \approx 5.3 \times 10^{-4} \text{ cm}/\text{V}s^{1/2} \).

It can be seen in Fig. 1 that the introduction of 120 ppm 1-NaphDATA results in transient currents being orders of magnitude smaller and corresponding transit times which are orders of magnitude longer than for the undoped \( \alpha \)-NPD. Nevertheless, the principal form of the current transients does not change. This indicates that nondispersive hole transport prevails, albeit trap controlled with a reduced mobility, which is compared to the values for the undoped material in Fig. 2. The mobilities of the doped sample are smaller by one order of magnitude compared to the values for the undoped material in Fig. 2. The zero field mobility is decreased by three orders of magnitude compared to the undoped material and the field dependence is more pronounced for the doped system.

Current transients for \( \alpha \)-NPD doped with 1160 ppm 1-NaphDATA, corresponding to a trap density of \( 1.16 \times 10^{18} \text{ cm}^{-3} \), are shown in Fig. 3. They exhibit featureless current decays when plotted on linear scales, while in a double logarithmic plot a kink can be observed, which is characteristic for dispersive transport. The physical difference to nondispersive transport can be seen in the relaxation process of the optically generated charge carriers to local thermal equilibrium within the DOS of organic semiconductors. For dispersive transport, thermal equilibrium is still not reached when the first charge carriers transit the film. Thus, the charge carriers decrease their mean hopping rate during transit, which leads to a decrease of the current amplitude with time. The kink in the current marks the transit time of the first and fastest charge carriers to arrive at the counter electrode. This transit time can be extracted from the intersection point of two linear fits to the current transients before and after the kink in a double-logarithmic plot. The mobilities calculated from those transit times are \( 6.4 \times 10^{-7} \text{ cm}^2/\text{V} \cdot \text{s} \) for 170 kV/cm and \( 6.6 \times 10^{-7} \text{ cm}^2/\text{V} \cdot \text{s} \) for 260 kV/cm, only an order of magnitude smaller than for the system with 120 ppm 1-NaphDATA at the same electric field. However, due to the dispersive nature of the transport, those values represent charge carriers moving rate during transit, which leads to a decrease of the current amplitude with time. The kink in the current marks the transit time of the first and fastest charge carriers to arrive at the counter electrode. This transit time can be extracted from the intersection point of two linear fits to the current transients before and after the kink in a double-logarithmic plot. The mobilities calculated from those transit times are \( 6.4 \times 10^{-7} \text{ cm}^2/\text{V} \cdot \text{s} \) for 170 kV/cm and \( 6.6 \times 10^{-7} \text{ cm}^2/\text{V} \cdot \text{s} \) for 260 kV/cm, only an order of magnitude smaller than for the system with 120 ppm 1-NaphDATA at the same electric field. However, due to the dispersive nature of the transport, those values represent charge carriers moving

\[ \mu^* \mu_0 = n_e/(n_e + n_i) = [1 + c \exp(\Delta E/kT)]^{-1}, \]

where \( c \) is the trap concentration, \( \Delta E \) the trap depth, \( k \) the Boltzmann constant, and \( T \) the temperature. The validity of Eq. (3) has been shown for organic crystals and solid solutions of small organic molecules in a polymeric binder. Since nondispersive transport is observed in undoped \( \alpha \)-NPD and \( \alpha \)-NPD doped with 120 ppm 1-NaphDATA, the moving charge carriers are in local thermal equilibrium. Therefore, Eq. (3) is used to calculate the trap depth from the zero field mobilities and the trap concentration. A value of \( \Delta E \) =406 meV results, which is within the energy difference between the reported ionization potentials for 1-NaphDATA of 5.0 eV (Ref. 13) and for \( \alpha \)-NPD between 5.2 and 5.7 eV. It is, however, about 20% smaller than the activation energy of 495 meV found by means of thermally stimulated currents. This difference may be explained by the fact that the model used here is based on a monoenergetic trap level and does not consider the energetic distribution of trap states. The result demonstrates that the above model for the case of nondispersive transport can also be applied to systems comprised solely of small molecules.
ing through the sample in nonequilibrium and, therefore, cannot truly be compared to the previously discussed mobilities derived from local thermal equilibrium.

The occurrence of dispersive transport upon increasing the trap concentration is due to the increased energetic disorder introduced by the trap states. The time it takes for optically generated charge carriers to relax to local thermal equilibrium increases with increasing width of the Gaussian DOS.\(^6\) Previously, the transition from nondispersive to dispersive transport in amorphous organic semiconductors has been studied as a function of temperature.\(^6\) There it was shown that this transition, which is observed upon reducing the temperature, occurs once the disorder parameter \(\tilde{\sigma} = \sigma / kT\) exceeds the critical value

\[
\tilde{\sigma}_c = \sqrt{A + B \log_{10}(d/cm)}, \quad (4)
\]

with the empirical constants \(A = 44.8\) and \(B = 6.7\). In the present work, however, \(\tilde{\sigma}\) is varied by changing the DOS of the organic semiconductor through trap states added by doping. With \(\sigma_c = kT\tilde{\sigma}_c\), the critical width for the transition to dispersive transport is calculated with Eq. (4) to be \(\sigma_{c,120 \text{ ppm}} = 117\) meV at room temperature for the 2.5-\(\mu\)m-thick sample doped with 120 ppm 1-NaphDATA. It is slightly smaller for the sample doped with 1160 ppm 1-NaphDATA, namely \(\sigma_{c,1160 \text{ ppm}} = 111\) meV, since the sample is only 1.2 \(\mu\)m thick.

On the other hand, the quantitative effect of adding traps to a Gaussian DOS has been derived for nondispersive transport.\(^6\) In this case, charge transport through a Gaussian DOS with the initial width \(\sigma_0\), to which trap states have been added, can be described by hopping through a single Gaussian DOS with an increased effective width \(\sigma_{\text{eff}}\). For hopping transport in a Gaussian DOS the mobility is\(^6\)

\[
\mu^{*} \propto \exp(-[2(\sigma/3kT)^{2}], \quad (5)
\]

Introduction into Eq. (3), with \(\mu^{*}\) and \(\sigma_0\) for the undoped system and \(\mu^{*}\) and \(\sigma_{\text{eff}}\) for the system with additional monenergetic trap states, yields

\[
\sigma_{\text{eff}} = \sqrt{\sigma_0^2 + \left(\frac{3}{2}kT\right)^2 \left[E/kT + \ln(c)\right]}, \quad (6)
\]

as long as \(c \exp(E/kT) \gg 1\). This condition is fulfilled for all devices investigated in the present work. The validity of Eq. (6) for nondispersive transport has been shown by a comparison of Monte Carlo simulations and experiments.\(^6\)

Under the premise that \(\sigma_{\text{eff}}\), which is deduced from nondispersive transport, can also predict the transition to dispersive transport, nondispersive transport prevails as long as \(\sigma_{\text{eff}}\) does not exceed \(\sigma_{\text{crit}}\). With \(\sigma_{\text{eff},120 \text{ ppm}} \leq \sigma_{c,120 \text{ ppm}}\) for the nondispersive transport observed in the moderately doped sample and with the trap depth derived above, Eq. (6) yields \(\sigma_{\text{crit}} \leq 60\) meV. \(\sigma_0\) is not known for \(\alpha\)-NPD in literature, but has been reported as 74 and 77 meV for \(N,N'\)-bis(3-methylphenyl)-\(N,N'\)-diphenyl-(1,1'-biphenyl)-4,4'-diamin (TPD),\(^17\) a small molecule similar to \(\alpha\)-NPD. Insofar a value of 60 meV seems realistic for \(\alpha\)-NPD. With \(\sigma_0 = 60\) meV, the effective width for the sample doped with 1160 ppm 1-NaphDATA is calculated to \(\sigma_{\text{eff},120 \text{ ppm}} = 130\) meV. This is far above \(\sigma_{c,1160 \text{ ppm}} = 111\) meV and, therefore, implies dispersive transport in accordance with the experimental result. From these considerations, the explanation of the observed transition from nondispersive to dispersive transport as a result of an increased energetic disorder through the addition of different trap concentrations is reasonable. We therefore suggest that the combination of the concepts of the critical width \(\tilde{\sigma}_c\) and the effective width \(\sigma_{\text{eff}}\) can be used to predict the transition from nondispersive to dispersive transport with increasing trap concentration.

In conclusion, hole transport through thermally evaporated films of the small molecule \(\alpha\)-NPD doped with hole traps by codeposition of 1-NaphDATA has been studied using an optical time-of-flight method. For \(\alpha\)-NPD doped with 120 ppm 1-NaphDATA nondispersive transport is observed for the undoped \(\alpha\)-NPD, but with a trap-controlled mobility reduced by orders of magnitude. The trap depth calculated from the reduction of mobility matches the difference in ionization potentials of \(\alpha\)-NPD and 1-NaphDATA, demonstrating that the used model holds for amorphous films consisting solely of small molecules. For further increased trap concentration, a transition to dispersive transport is observed. This can be understood in the context of hopping transport in an amorphous organic semiconductor with a Gaussian DOS by combining the concepts of a critical width for the transition to dispersive transport and an effective width of a DOS broadened by added trap states.

The authors would like to thank Sensient Imaging Technologies for donating the organic materials and the German Research Foundation (DFG) for financial support of one of the authors (A.F.) through Collaborative Research Center SFB 595.

---


\(^{9}\)P. M. Borsenberger and D. Weiss, *Organic Photo receptors for Xerography* (Eastman Kodak, Rochester, 1998).


