Electron transport and electrical properties in a high-mobility n-type conjugated polymer

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The electron transport and electrical properties in a high-mobility n-type copolymer poly{[N,N'-bis(2-octyldodecyl)--naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diy1]-alt-5,5'-(2,2'-dithiophene)}[P(NDI2OD-T2),PolyeraActivInk™ N2200] are investigated. It is found that the thickness dependent current density versus voltage ($J-V$) characteristics of N2200 electron-only devices cannot be well described by using the conventional mobility model. However, the thickness dependent and temperature dependent $J-V$ characteristics of N2200 electron-only devices can be accurately described by using our recently introduced improved mobility model only with a single set of parameters. For the material studied, we find the width of the Gaussian density of states $\sigma = 0.083$ eV and lattice constant $a = 0.8$ nm. The width of the DOS is considerably smaller than usually obtained for conjugated polymers, indicating a low degree of energetic disorder and small temperature activation. Furthermore, we show that too large or too small values of the boundary carrier density lead to incorrect $J-V$ characteristics.

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1. Introduction

Conjugated polymers form a particularly interesting class of organic semiconductors due to their potential for low-cost, high-throughput, flexible, large-area, lightweight printed electronics. For most conjugated polymers, electron and hole transport is highly unbalanced in electronic devices [1, 2]. In several functional devices fabricated from conjugated polymers, hole currents show trap-free space-charge-limited behavior [1], whereas electron currents are largely reduced by the presence of charge trapping [3-5]. It has been shown that conducting polymers with an electron affinity lower than ~3 eV have a strong tendency to be oxidized by oxygen or water [6]. Such oxidative processes are known to create electron-accepting defects. Consequently, polymeric structures with increased electron affinity should dramatically reduce the trap density to enable efficient electron transport [7]. Recently, a novel high-mobility electron-transporting polymer, poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diy1]-alt-5,5'-(2,2'-dithiophene)}[P(NDI2OD-T2), PolyeraActivInk™ N2200], was developed [8]. Apart from its high electron mobility, this polymer is particularly interesting because of the location of the lowest unoccupied molecular orbital (LUMO) at ~4 eV and an optical bandgap of 1.45 eV [9]. This implies that the LUMO is low enough for stable, trap-free electron transport. These characteristics make N2200 a promising candidate for organic electronic devices such as light-emitting diodes (OLEDs), field-effect transistors (OFETs) or solar cells (OSCs).

Understanding charge transport and availability of physical models in organic semiconductors is of fundamental importance for further advancement of electronic and optoelectronic devices. In particular, it is crucial to understand how the charge-carrier mobility μ depends on various parameters of the system. In past decades, the dependence of μ on the temperature T and electric field E has been extensively investigated [10-13]. Recently, it was recognized that the importance of another parameter had been overlooked: the charge-carrier density p [14, 15]. From a numerical solution of the master equation for hopping transport in a disordered energy system, a complete description of charge transport has been developed by Pasveer et al. that determines the dependence of the mobility on the temperature, carrier density, and electric field, which is known as the "extended Gaussian disorder model" (EGDM) [16]. However, it should be noted that their model, having a non-Arrhenius temperature dependence $\ln(\mu) \propto 1/T^2$, can only well describe charge transport at low carrier densities, whereas at high carrier densities, it becomes unsatisfactory. In order to better describe charge transport, we proposed an improved unified description of the temperature, carrier density, and electric field dependence

of the mobility based on both the Arrhenius temperature dependence $\ln(\mu) \propto 1/T$ and non-Arrhenius temperature dependence [17]. It has been demonstrated that the improved model is more applicable for organic semiconductors than the EGDM, especially at high carrier density and high electric field [18, 19]. Although accurate theoretical descriptions are thus available for the improved mobility model, its applicability to electron transport in organic materials has not yet been fully established.

In this paper, electron transport and electrical properties in N2200 are investigated. Firstly, we perform a detailed analysis of the current density versus voltage ($J-V$) characteristics for N2200 electron-only devices by using the conventional mobility model and our improved model, respectively. Subsequently, we calculate and analyze the variation of the $J-V$ characteristics with the boundary carrier density for N2200 by using the improved model. In Section 2 the improved model is presented. In Section 3 the systematic study of electron transport and electrical properties for N2200 is given. Section 4 contains a summary and conclusions.

2. Model

The improved unified description of the temperature T, carrier density p, and electric field E dependence of the mobility μ based on both the Arrhenius temperature dependence and non-Arrhenius temperature dependence can be described as follows [17]:

$$\mu(T,p) = \mu_0(T)\exp[\frac{1}{2}\left(\hat{\sigma}^2-\hat{\sigma}\right)\left(2pa^3\right)^{\delta}], \quad (1a)$$

$$\mu_0(T) = \mu_0 c_1 \exp(c_2\hat{\sigma}-c_3\hat{\sigma}^2), \quad (1b)$$

$$\delta \equiv 2\frac{\ln(\hat{\sigma}^2-\hat{\sigma})-\ln(\ln 4)}{\hat{\sigma}^2}, \ \mu_0 \equiv \frac{a^2\nu_0 e}{\sigma}, \quad (1c)$$

with $c_1 = 0.48\times10^{-9}$, $c_2 = 0.80$, and $c_3 = 0.52$, where $\mu_0(T)$ is the temperature dependent mobility in the limit of zero electric field and charge-carrier density, $\hat{\sigma} \equiv \sigma/k_BT$ is the dimensionless disorder parameter, σ is the width of the Gaussian density of states (DOS), a is the lattice constant, e is the charge of the carriers, and ν_0 is the attempt frequency.

$$\mu(T,p,E) = \mu(T,p)^{g(T,E)}\exp[c_4\left(g(T,E)-1\right)], \quad (2)$$

$$g(T,E) = [1+c_5(Eea/\sigma)^2]^{-1/2}, \quad (3)$$

where $g(T,E)$ is a weak density dependent function, c_4 and c_5 are weak density dependent parameters.

$$c_4 = d_1 + d_2\ln(pa^3) \quad (4a)$$

$$c_5 = 1.16 + 0.09\ln(pa^3) \quad (4b)$$

$$d_1 = 28.7 - 36.3\hat{\sigma}^{-1} + 42.5\hat{\sigma}^{-2} \quad (5a)$$

$$d_2 = -0.38 + 0.19\hat{\sigma} + 0.03\hat{\sigma}^2 \quad (5b)$$

Using the above results, the $J-V$ characteristics and other electrical properties of conjugated polymers can be obtained by numerically solving the coupled equations.

$$J = p(x)e\mu(T, p(x), E(x))E(x), \quad (6a)$$

$$\frac{dE}{dx} = \frac{e}{\varepsilon_0\varepsilon_r}p(x), \quad (6b)$$

$$V = \int_0^L E(x)dx, \quad (6c)$$

where x is the distance from the injecting electrode, L is the polymer layer thickness sandwiched between two electrodes, ε_0 is the vacuum permeability, and ε_r is the relative dielectric constant of the conjugated polymer.

3. Results and discussion

Measurements on electron transport of polymer N2200 have been carried out recently by Wetzelaer et al [20]. In their report, single-carrier electron-only devices were fabricated by using the following structure: Al (bottom electrode) | N2200 | Cs_2CO_3 | Al (top electrode). Cesium carbonate (Cs_2CO_3) was utilized as an efficient electron injection layer in the polymer diodes. The current in such a single-carrier device will be limited by the buildup of uncompensated charges, giving rise to a space-charge limited current (SCLC). The well-known expression for the SCLC in electronic devices has been obtained by Mott and Gurney [21], given by

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{L^3}, \quad (7)$$

where J is the current density, ε is the permittivity, μ is the charge-carrier mobility, V is the applied voltage, and L is the layer thickness. The thickness dependent $J-V$ characteristics of N2200 electron-only devices are displayed in Fig. 1. As can be observed in this figure, the currents exhibit a quadratic dependence on voltage and the experimental data from Ref. [20] can be well described by Eq. (7) for all layer thicknesses in the low-field regime. The extracted value for the zero-field mobility is 5 $\times$ 10^{-8} m^2/V s for all layer thicknesses. However, at higher applied fields, the current starts to deviate from the quadratic voltage dependence and the experimental data cannot be well described by Eq. (7) for all layer thicknesses. This indicates that the thickness dependent $J(V)$ curves cannot be described consistently using the conventional mobility model. This enhancement

of the SCLC arises from the carrier density dependence of the mobility [22, 23]. This suggests that the dependence of the mobility on the carrier density should be taken into account when describing charge transport in conjugated polymers.

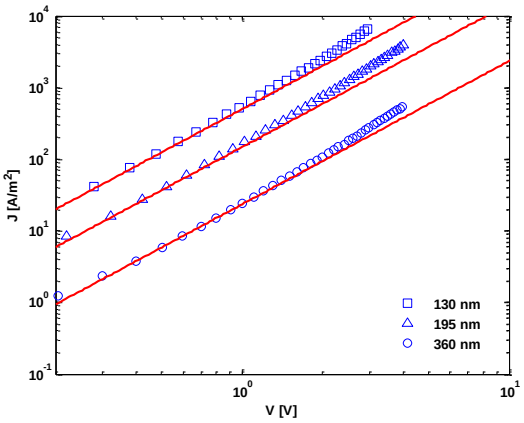

Fig. 1. Thickness dependent $J-V$ characteristics of N2200 electron-only devices. The symbols are experimental data from Ref. [20]. The lines are fits to the experimental data, calculated from Eq. (7)

As a next step, we perform a systematic study of electron transport and electrical properties for N2200 by using the improved mobility model as described in section 2. The solution of the coupled equations describing the SCLC with the improved model and the experimental $J-V$ measurements from Ref. [20] for N2200 electron-only devices with various layer thicknesses and various temperatures are displayed in Fig. 2 and Fig. 3, respectively. It can be seen from the figures that the thickness dependent and temperature dependent $J-V$ characteristics of N2200 electron-only devices can be excellently described using a single set of parameters, $a = 0.8$ nm, $\sigma = 0.083$ eV, and $\mu_0 = 2000$ m^2/V s. The parameters a, σ, and μ_0 are determined in such a way that an optimal overall fit is obtained. It is clear that our calculated results are in good agreement with experimental data. This suggests that the improved mobility model is suitable to study the $J-V$ characteristics of N2200, and captures the physical essence of electron transport in this polymer. As for the parameters, the value of the lattice constant a is significantly smaller than the result obtained by Wetzelaer et al [20]. The width of the DOS is considerably smaller than usually obtained for conjugated polymers [16, 18], indicating a low degree of energetic disorder of the LUMO. The observation of weak disorder is in agreement with the high electron mobility values obtained. In addition, the weak disorder gives rise to small temperature activation for charge transport. The good agreement of the numerical simulations based on the improved model with experimental $J-V$ characteristics also shows that the dependence of the mobility on the electric field, carrier density, and temperature needs to be taken into account for describing electron transport in conjugated polymers.

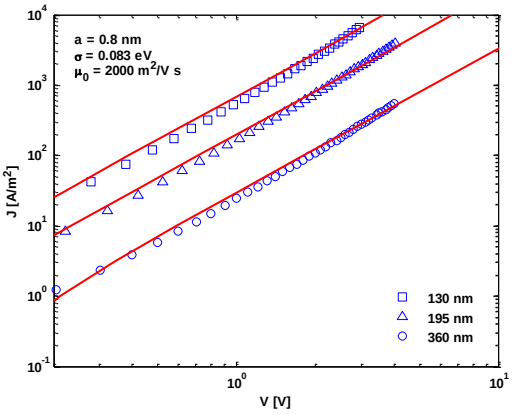

Fig. 2. Thickness dependent $J-V$ characteristics of N2200 electron-only devices. The symbols are experimental data from Ref. [20]. The lines are calculated results from Eqs. (1) – (6)

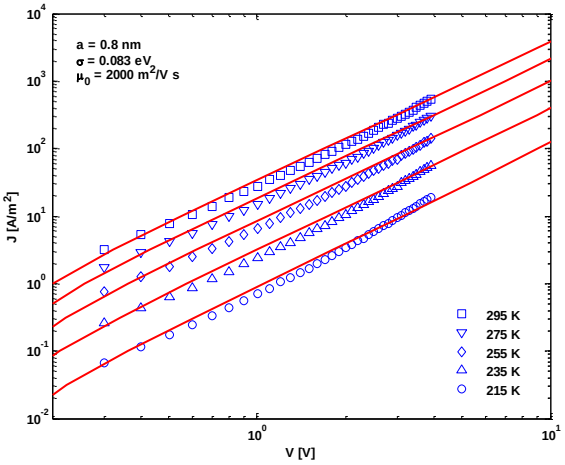

Fig. 3. Temperature dependent $J-V$ characteristics of an N2200 electron-only device with a layer thickness of 360 nm. The symbols are experimental data from Ref. [20]. The lines are calculated results from Eqs. (1) – (6)

The variation of $J-V$ characteristics with the boundary carrier density $p(0)$ (the carrier density at the interface) at low temperature and room temperature for N2200 electron-only devices is plotted in Fig. 4. The figure shows that the voltage is an increasing function of the current density, and the variation of voltage with $p(0)$ is dependent on current density. The voltage decreases with increasing $p(0)$ for relatively small $p(0)$, and also increases with increasing $p(0)$ for sufficiently large $p(0)$. However, it is worth noting that the $V - p(0)$ curves are fairly flat in the middle region. This means that the voltage is almost independent on $p(0)$ in this region. As a result, too large or too small values of the boundary

carrier density lead to incorrect $J-V$ characteristics, whereas the values of the boundary carrier density in the middle region can achieve reasonable results. Now we analyze the physical reason of variation in this figure. In the region of small $p(0)$, the carrier concentration in bulk material is small, and the impedance and voltage are relatively large. As $p(0)$ increasing in the middle region, the injection of carriers near the interface and the drain into bulk material reach equilibrium, the $J-V$ characteristics move into the Ohmic region, and the $V-p(0)$ curves become flat. Moreover, it is clear from the figure that in order to reach the same current density J at the same $p(0)$, the stronger electric field and corresponding larger voltage are needed at low temperature than that at high temperature. As for this point, it is generally agreed that the thermal excitation and the energy of the motion of carriers in conjugated polymers are relatively weaker at low temperature than those at high temperature. Therefore, we conclude that the carrier density dominates the space-charge limited $J-V$ characteristics at room temperature, whereas the electric field becomes more important at low temperature. This result is fully consistent with that of Pasveer et al. [16] and Tanase et al. [23].

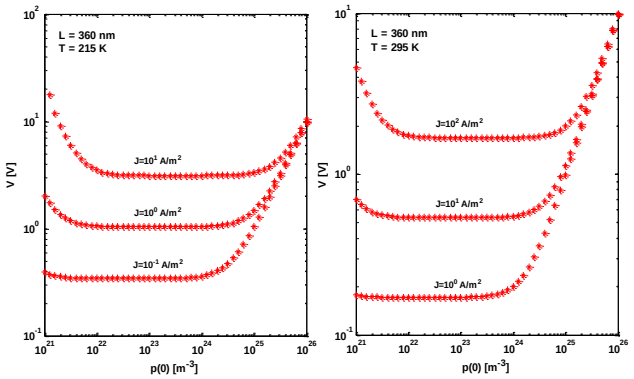

Fig. 4. Theoretical results of the voltage versus the boundary carrier density for N2200 layer at 215 K and 295 K, respectively. Different lines correspond to different current density values

4. Summary and conclusions

In conclusion, electron transport and electrical properties for polymer N2200 have been investigated. We demonstrate that the thickness dependent $J-V$ characteristics of N2200 electron-only devices cannot be well described by using the conventional mobility model. We find that the thickness dependent and temperature dependent $J-V$ characteristics of N2200 electron-only devices can be accurately described by using the improved mobility model only with a single set of parameters, $a=0.8$ nm, $\sigma=0.083$ eV, and $\mu_0=2000$ m^2/V s. The width of the DOS is smaller than usually obtained for conjugated polymers, indicating a low degree of energetic disorder and small temperature activation. It is shown that the improved model is suitable for N2200 and the carrier density dependence of the mobility is significant for describing electron transport in conjugated polymers. In addition, it is shown that too large or too small values of the boundary carrier density lead to incorrect $J-V$ characteristics. These results open the prospect that the improved model can also provide the appropriate framework for describing electron transport in conjugated polymers.

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