Temperature- and Field-dependent electron and hole mobilities in polymer light-emitting diodes

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We have studied the transport properties of electron- and hole-dominated MEH-PPV, poly(2-methoxy,5-(2′-ethyl-hexoxy)-*p*-phenylene vinylene), devices in the trap-free limit and have derived the temperature-dependent electron and hole mobilities ($\mu = \mu_0 e^{\gamma \sqrt{E}}$) from the space-charge-limited behavior at high electric fields. Both the zero-field mobility μ_0 and electric-field coefficient γ are temperature dependent with an activation energy of the hole and electron mobility of 0.38 ± 0.02 and 0.34 ± 0.02 eV, respectively. At 300 K, we find a zero-field mobility μ_0 on the order of $1 \pm 0.5 \times 10^{-7}$ cm^2/V s and an electric-field coefficient γ of $4.8 \pm 0.3 \times 10^{-4}$ (m/V)$^{1/2}$ for holes. For electrons, we find a μ_0 an order of magnitude below that for holes but a larger γ of $7.8 \pm 0.5 \times 10^{-4}$ (m/V)$^{1/2}$. Due to the stronger field dependence of the electron mobility, the electron and hole mobilities are comparable at working voltages in the trap-free limit, applicable to thin films of MEH-PPV. © *1999 American Institute of Physics.*
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Since the discovery of electroluminescence in polymers early in this decade,[1] mechanisms for charge transport in polymer semiconductors have been actively debated. Understanding transport in polymer light-emitting diodes (PLEDs) has been complicated by the presence of both electrons and holes in working devices for which complete analytical models do not exist. In addition, inelastic and elastic tunneling contacts[2] combined with extrinsic traps may exist for one or both carriers further complicating interpretation of the transport behavior. Electrons are particularly sensitive to traps formed during processing, atmospheric contamination and molecular diffusion, making measurements of the intrinsic electron mobility difficult. Consequently, most polymers semiconductors are considered to be dominantly hole transporting materials.

In this letter, we present results in the trap-free limit for *both* electron- and hole-dominated MEH-PPV, poly(2-methoxy,5-(2′-ethyl-hexoxy)-*p*-phenylene vinylene), based devices as a function of temperature. Using nearly ohmic single-carrier injecting contacts, we observe space-charge-limited current for both types of devices above moderate voltages (>4 V). While the zero-field electron mobility is an order of magnitude lower than the hole mobility, a stronger electric-field dependence for electrons results in similar mobilities (and carrier densities in bipolar devices) for electrons and holes at working voltages. This result explains the changes in quantum efficiency with temperature and Schottky barrier observed for MEH-PPV-based PLEDs. Moreover, it indicates that electrons can be as mobile as holes in polymer electroluminescent materials.

The devices were made in an inert atmosphere as described previously[3] using a variety of injecting anodes. The polymer semiconductor MEH-PPV, poly(2-methoxy,5-(2′-ethyl-hexoxy)-*p*-phenylene vinylene), has a band gap of 2.1 eV and is known to have a highest occupied molecular orbital (HOMO) consistent with 5.3 eV and a lowest unoccupied molecular orbital (LUMO) of 3.0 eV.[4] Both doped-polyaniline (PAni) (work function 5.0 eV)[3] and Au (work function 5.1 eV) form nearly ohmic hole-injecting contacts to MEH-PPV. Metallic Ca (2.9 eV) forms a nearly ohmic electron-injecting contact. We used poorly injection Al (4.2 eV) with PAni to form our hole-dominated devices. For the electron-dominated devices, we found that commercially processed TiN (3.9 eV) as an anode enabled the reproducible measurement of space-charge-limited electron current; devices made with Ca or Al as an anode were trap dominated as observed by others.[5,6] The devices were heat sunk to a copper block inside an inert atmosphere and the measurements were done in an Oxford Cryostat. No sample aging was observed over the length of each experiment. In order to compare the current densities and mobilities of electron, hole, and double-carrier injected devices, the built-in potential, 1.8 V for PAni/Ca, 0.8 V for PAni/Al and 1.0 V for TiN/Ca, is subtracted from all voltage scales.[7]

In Fig. 1, we show the dependence of the current density with average electric field for the bipolar (PAni/Ca), electron-dominated (TiN/Ca) and hole-dominated (PAni/Al) MEH-PPV-based devices at only 200 K (closed symbols) and 300 K (open symbols) for clarity. The electron-dominated current (squares) is below the hole-dominated current (circles) at 300 K; however, as the temperature is lowered and the electric-field increased, the electron current becomes comparable and even exceeds the hole current. Both single-carrier currents are less than half of the double-

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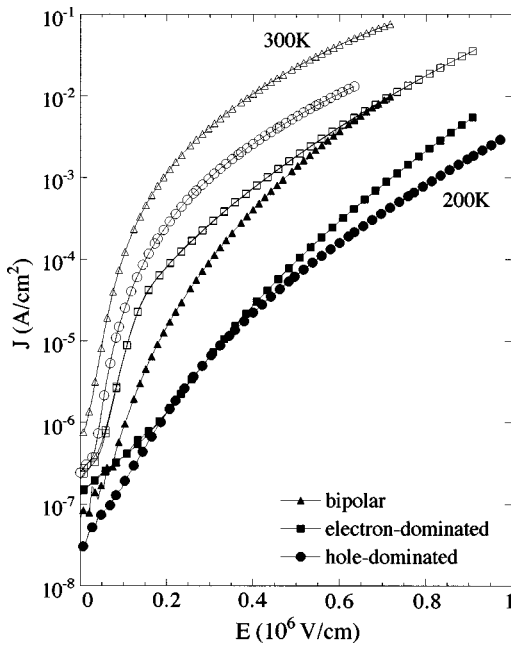
FIG. 1. Current density vs electric field for bipolar (triangles), electron (squares), and hole-dominated (circles) MEH-PPV-based devices at 200 K (closed symbols) and 300 K (open symbols). Anodes/cathodes for the devices are PAni/Ca, TiN/Ca, and PAni/Al for the bipolar, electron- and hole-dominated devices, respectively. The bipolar and hole-dominated devices are 145 nm thick and the electron-dominated device is 120 nm thick.
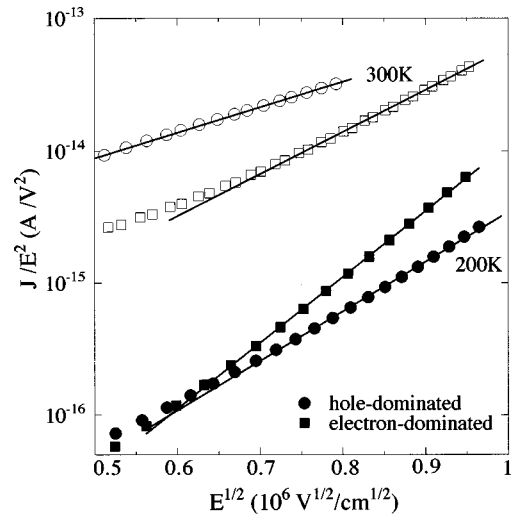

FIG. 2. Space-charge-limited current for the electron (squares)- and hole (circles)-dominated MEH-PPV-based devices at 200 K (close symbols) and 300 K (open symbols). Both electrons and holes are space charge limited at working voltages. The lines are fits to space-charge-limited behavior.

carrier current reflecting the efficiency of bimolecular recombination in MEH-PPV-based devices.

These data can be understood by considering the trap-free space-charge-limited current density for a single carrier given by

$$J = 9/8\epsilon\mu E^2/L, \tag{1}$$

where E is the electric field across the device and L is the thickness of the active polymer.[8] The carrier mobility μ is described by a Poole–Frenkel-like form,[9]

$$\mu = (\mu_* e^{-\Delta/kT}) e^{\gamma\sqrt{E}}, \tag{2}$$

where Δ is the activation energy, k the Boltzmann's constant, μ_* the mobility prefactor, and γ the electric-field coefficient to the mobility due to the interaction between charge carriers and randomly distributed permanent dipoles in semiconducting polymers.[10] The quantity in parenthesis in Eq. (2) is field independent and is usually identified as the zero-field mobility μ_0. Combining Eqs. (1) and (2),[11] the electric-field dependence of the current shown in Fig. 2 indicates that *both* the electron and hole carrier densities are space charge limited above 4 V. The space charge is reduced in double-carrier devices due to neutralization leading to significant enhancements in current densities as observed in Fig. 1. We note that the space-charge-limited form is robust in our MEH-PPV devices; attempts to fit the data to forms involving inelastic or elastic tunneling or trap-controlled current yield either unreasonable parameters or are over a sufficiently small range to make such alternative interpretations dubious. Preliminary transient transport measurements shows essentially trap-free behavior in MEH-PPV over a wide range of thicknesses.[12]

Further analysis of Fig. 2 reveals that the electric-field dependence of the mobility μ is significantly stronger for electrons than for holes. We plot the dependence of the

electric-field coefficient γ on temperature for both electron and holes in the bottom half of Fig. 3.[13] The coefficient γ can be written according to the empirical relation:

$$\gamma = (1/kT - 1/kT_0)B \tag{3}$$

with B and T_0 constant.[14] We can solve for both quantities from our measurements. For the holes, we find that $B = 2.3 \pm 0.2 \times 10^{-5}$ eV(m/V)$^{1/2}$ and $T_0 = 600 \pm 90$ K, while for the electrons, we find $B = 2.6 \pm 0.4 \times 10^{-5}$ eV(m/V)$^{1/2}$ and $T_0 = 880 \pm 150$ K. The values for the hole-dominated devices
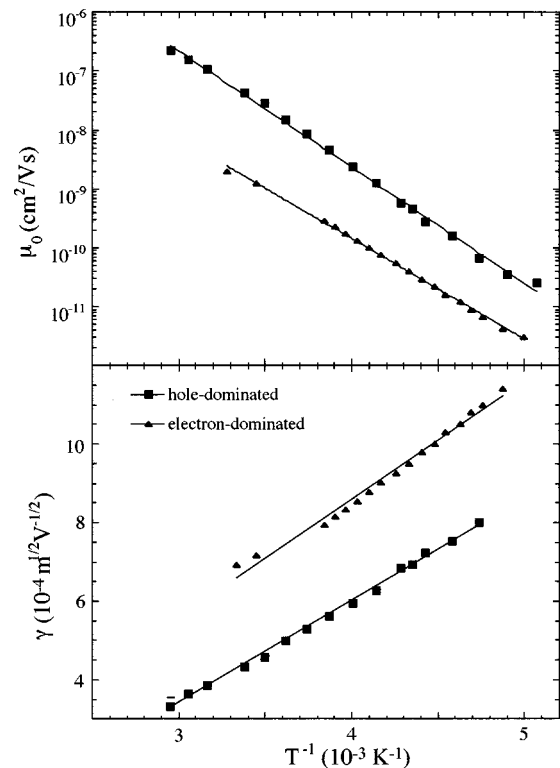

FIG. 3. Zero-field mobility μ_0 (top) and the electric-field prefactor γ (bottom) vs temperature for both the electron (squares)- and hole (circles)-dominated devices.

are comparable to what was obtained previously in another PPV-derivative hole-only derivative hole-only device.[6]

In Fig. 3, the zero-field mobility is logrithmically graphed on the same temperature scale revealing thermally activated behavior. As with γ, we cannot distinguish between $1/kT$ and $1/(kT)^2$ over our limited temperature range;[14] fitting to $1/kT$, the zero-field mobility thermal activation energy gap Δ is 0.38 ± 0.02 and $0.34 \, \text{eV} \pm 0.02 \, \text{eV}$ for holes and electrons, respectively. We can solve for the energetic disorder[10] and find values of $80 \pm 10 \, \text{meV}$ for holes and $70 \pm 10 \, \text{meV}$ for electrons, very comparable to molecularly doped charge transport materials.[10] Our zero-field mobilities and activation energies are slightly lower but similar to what has been observed by Blom *et al.* for hole-only devices made with ITO with Au electrodes.[15] For our Au devices, we observe almost identical behavior to the Al at low temperatures. At higher temperatures, the Au devices are very sensitive to electrode deposition conditions; however, with proper cleaning and annealing comparable space-charge-limited behavior is observed.[16]

The changes in the intrinsic single-carrier densities and mobilities with temperature explain many characteristics of polymer light-emitting diodes, particularly MEH-PPV-based devices. The increase in the quantum efficiency in MEH-PPV upon cooling is due to the improvement in charge balance. The theoretical limit for MEH-PPV near 2.5% quantum efficiency for singlet radiative recombination is reached at the same temperature, namely, 200 K, where the electron and hole currents are comparable.[17] Since both carriers are mobile, the recombination efficiency is dictated primarily by injected carrier densities i.e., by electrode barriers. By adjustment of the barrier heights, at the level of 0.1 eV or less, quantum efficiencies close the theoretical maximum can be achieved.[16]

Moreover, these results suggest that high current densities in polymer LEDs are limited primarily by space-charge affects for both the electrons and holes. Therefore, to achieve very bright devices with high densities, on the order of kA/cm^2 estimated to be needed for electrically pumped stimulated emission, for example, the space-charge effects must be reduced. In materials such as MEH-PPV where the recombination efficiency is already near unity, this can only be accomplished by increasing the intrinsic carrier mobility, by modifying the dielectric constant, or by electrically pulsing the device at repetition times longer than the recombination time. The carrier mobility can be improved by aligning the polymer backbone, but such ordering is known to lead to photoluminescence quenching and reduced efficiency. The dielectric constant may be effectively enhanced by blending the system with a highly polarizable material; this affect may be occurring in polymer nanoparticle composites.[17]

In conclusion, current densities for both electrons and holes in MEH-PPV have been shown to follow trap-free space-charge-limited behavior. The electric-field and temperature dependencies of the mobilities result in comparable electron and hole currents in operating bipolar devices at room temperature. MEH-PPV is a good transporter of both electrons and holes.

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