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The transport properties of electrons and holes in poly(dialkoxy-*p*-phenylene vinylene) (PPV) are investigated by current–voltage measurements using Ca as an electron and indium-tin-oxide as a hole injecting contact. Both the electron and hole currents are dominated by the bulk conduction properties of the PPV, in contrast to previous reports. The hole current is governed by bulk space-charge limited conductivity and a hole mobility of 0.5×10^{-6} cm^2/V s is determined. The electron current is strongly reduced by the presence of traps with a total density of 10^{18} cm^{-3}. © *1996 American Institute of Physics.* [S0003-6951(96)03423-7]

As a result of both easy processing and mechanical flexibility polymer light-emitting diodes (LEDs) are presently considered as suitable candidates for large-area applications.[1,2] Attention has especially been focused on poly(phenylene vinylene) (PPV) derivatives which have an external conversion efficiency of larger than 1% photons/electron. In order to optimize the device efficiency of polymer LEDs a balanced charge injection and charge transport should be achieved.[3]

It has been proposed by Parker[4] that the current-density–voltage (J–V) characteristics of polymer LEDs are controlled by charge injection. At high electric fields ($>5 \times 10^5$ V/cm) the J–V characteristics are determined by Fowler–Nordheim tunneling of both electrons and holes through contact barriers arising from the band offset between the polymer and the electrodes. However, quantitatively at these high fields the predicted Fowler–Nordheim currents exceed the experimentally observed currents by several orders of magnitude. Furthermore, at low fields the tunneling model was found not to be applicable to the experimental J–V characteristics, which has been attributed to the contribution of thermionic emission to the current[4] and to band-bending effects at the interface.[5]

On the other hand, from time-of-flight measurements Antoniades *et al.*[6] determined deep trapping products ($\mu\tau$) for electrons and holes in PPV. These experiments show that electrons, in contrast to holes, are severely trapped in PPV, which results in an unbalanced electron and hole transport. Such a severe electron trapping will certainly affect the J–V characteristics and efficiency of polymer LEDs. It is crucial for the understanding and optimization of polymer LEDs to obtain an answer to the question of whether the device characteristics of polymer LEDs are controlled by unbalanced injection[4] or transport.[6]

So far, no adequate description of the J–V behavior of polymer LEDs has been provided which includes both injection and bulk transport properties. In the present study, we provide a consistent description of the J–V characteristics of PPV devices. Using indium-tin-oxide (ITO) for hole injection and Ca for electron injection, we find that the J–V characteristics are dominated by the bulk-conduction properties of the PPV. The hole current is space-charge limited,

whereas electrons in our devices are severely trapped. Such a bulk-limited behavior is expected for injection barriers smaller than 0.2 V.

The devices in our study consist of a single polymer layer sandwiched between two electrodes on top of a glass substrate. The polymer we use is soluble poly(dialkoxy-*p*-phenylene vinylene),[7] shown in the inset of Fig. 1 with $R1 = CH_3$ and $R2 = C_{10}H_{21}$, which is spin coated on the patterned bottom electrode. In order to study the transport properties of the holes an ITO bottom contact is used as hole injector and an evaporated Au contact as a top electrode. In these so-called hole-only devices[4] the work functions of both electrodes are close to the valence band of PPV. In Fig. 1 the J–V characteristics of several ITO/PPV/Au hole-only devices are presented. From the slope of the log$J$–log$V$ plot we observe that the current density J depends quadratically on the voltage V. This behavior is characteristic for space-charge limited current (SCLC) in which case:[8]

$$J = \frac{9}{8}\, \epsilon_0 \epsilon_r \mu_p \frac{V^2}{L^3},\tag{1}$$

with $\epsilon_0 \epsilon_r$ permittivity of the polymer, μ_p the hole mobility, and L the thickness of the device. Assuming $\epsilon_r = 3$, we find that the J–V characteristics of our devices, with $L = 0.13, 0.3$, and 0.7 μm, respectively, are well described by Eq. (1) using $\mu_p = 0.5 \times 10^{-6}$ cm^2/V s. The observed mobility is larger than the field-effect mobility of 1×10^{-7} cm^2/V s obtained in a PPV MISFET.[9] The absence of a sharp increase in the current (trap-filled limit)[8] indicates that the hole transport in our PPV can be regarded as trap free. At high electric fields ($>3 \times 10^5$ V/cm) a gradual deviation from the square law occurs, probably due to an increase of the mobility, a subject which is presently under investigation. The importance of the observation of space-charge limited current in our hole-only devices is that it clearly demonstrates that the hole current is bulk limited and not injection limited, as proposed before.[4]

The transport properties of electrons are investigated using an electron-only device consisting of a PPV layer sandwiched between two Ca electrodes, which have a work function close to the conduction band of PPV. In Fig. 2 the J–V characteristic for $L = 0.3$ μm is shown together with the SCLC according to Eq. (1), which describes the hole transport. The electron current is smaller than the hole current, especially at low bias where the difference amounts to three
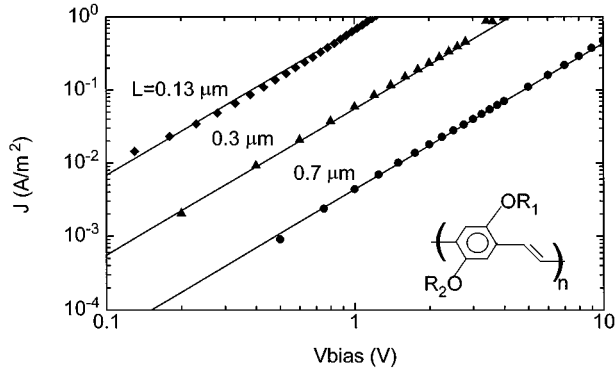
FIG. 1. Experimental and calculated (solid lines) J–V characteristics of ITO/PPV/Au hole-only devices with thicknesses $L=0.13$ μm (squares), 0.30 μm (triangles), and 0.70 μm (dots). The hole transport for all samples is described by SCLC [Eq. (1)] with a hole mobility $\mu_p = 0.5 \times 10^{-6}$ cm^2/V s and a dielectric constant $\epsilon_r = 3$. The inset shows the PPV used in this study with $R_1 = CH_3$ and $R2 = C_{10}H_{21}$.

orders of magnitude. In the J–V plot of the electron-only device two different regimes are discriminated: Below a critical voltage $V_c (<9$ V) the electron current depends linearly on the bias voltage. For this Ohmic regime, one expects:

$$J = n_0 q \mu_n \frac{V}{L},\qquad(2)$$

with electron mobility μ_n, and equilibrium electron density n_0. For voltages above V_c the electron current strongly increases. The occurrence of an abrupt increase of the current at a certain critical voltage V_c is characteristic for an insulator with traps.[8] For trap levels located at a single energy this trap-filled limit (TFL) is an extremely sharp transition, at which the current directly switches to the SCLC. The more gradual increase, as observed in Fig. 2, points to a distribution of trap-level energies. Actually, this is what one would expect for a disordered system, such as a polymer. The J–V characteristic in Fig. 2 is well described using an exponential distribution of traps ($E < E_c$):
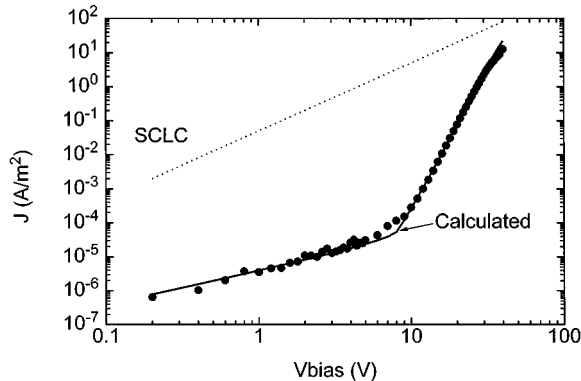

FIG. 2. Experimental (dots) and theoretical (solid line) J–V characteristic of a Ca/PPV/Ca electron-only device with a thickness $L=0.31$ μm. The theoretical curve is obtained assuming an exponential trap distribution with a trap density $N_t = 5 \times 10^{17}$ cm^{-3}, a trap distribution parameter $T_t = 1500$ K, and an equilibrium electron density $n_0 = 1.5 \times 10^{11}$ cm^{-3}. The dashed line gives the (hole) SCLC, according to Eq. (1).

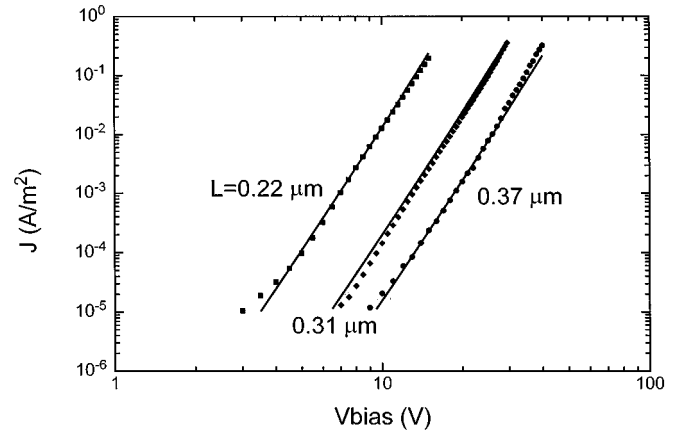FIG. 3. Thickness dependence of the electron only J–V characteristics at $L=0.22$, 0.31, and 0.37 μm. The solid lines represent the predicted J–V characteristics according to Eq. (4). For this set of samples the trap density $N_t = 1 \times 10^{18}$ cm^{-3}.

$$n_t(E) = \left(\frac{N_t}{kT_t}\right)\exp\left(\frac{E - E_c}{kT_t}\right),\qquad(3)$$

with $n_t(E)$ the trap density of states at energy E, E_c the energy of the conduction band, N_t the total density of traps, and kT_t an energy characterizing the trap distribution. The trap distribution (3) implies for the J–V characteristic in the TFL regime[8] (>9 V):

$$J = N_c q \mu_n \left(\frac{\epsilon_0 \epsilon_r}{q N_t}\right)^r \frac{V^{r+1}}{L^{2r+1}} C(r),\qquad(4)$$

with $r = T_t/T$, N_c the effective density of states in the conduction band, and $C(r) = r^r (2r+1)^{r+1}(r+1)^{-r-2}$. Assuming the effective mass $m^* = 1$, N_c amounts to 2.5×10^{19} cm^{-3}.

The complete J–V characteristic in Fig. 2 is then determined by four parameters: the carrier mobility μ_n, the equilibrium density n_0, the trap density N_t, and the trap distribution parameter T_t. The latter follows directly from the slope of the log$J$–log$V$ characteristic in the TFL regime, according to Eq. (4), which yields $T_t = 1500$ K. Furthermore, from the slope in the Ohmic region the product $u_n n_0$ can be determined, according to Eq. (2). Assuming $\mu_p = \mu_n$,[10] we find $n_0 = 1.5 \times 10^{11}$ cm^{-3}. Finally, it follows from Eq. (4) that $N_t = 5 \times 10^{17}$ cm^{-3}. Using these parameters we find good agreement between our experimental and theoretical results, as shown in Fig. 2.

It should be noted from Eq. (4) that the trap distribution parameter T_t not only determines the slope of the log$J$–log$V$ plot, but also the thickness dependence in the TFL regime. In Fig. 3 the experimental as well as predicted J–V characteristics of another set of electron-only devices are shown for $L=0.22$, 0.31, and 0.37 μm. The calculations with $N_t = 1 \times 10^{18}$ cm^{-3} and $n_0 = 1 \times 10^{10}$ cm^{-3}, are in excellent agreement with the experimental results. The observed thickness dependence, which is characteristic for an exponential trap distribution, clearly proves that the electron current is determined by the bulk-transport properties of the PPV.
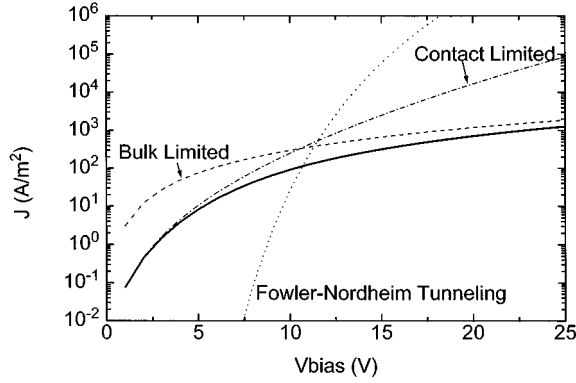
FIG. 4. Calculated $J-V$ characteristic (solid line) for a device with thickness $L=0.1$ μm, an injection barrier height $\phi_{b0}=0.35$ V, a mobility μ $=10^{-6}$ cm^2/V s, and a dielectric constant $\epsilon_r=3$. For comparison, the bulk limited SCLC [dashed line, Eq. (1)] as well as the diffusion limited injection [dashed–dotted line, Eqs. (4) and (5)] and the Fowler–Nordheim current (dotted line), assuming $F(x)=F(0)=V/L$ is also included.

Thus, our results confirm the severe trapping of electrons as observed in time-of-flight measurements by Antoniades *et al.*[5]

So far, we have demonstrated that both the electron and hole current are controlled by the bulk conduction properties of the polymer. As a result the injection barriers at the ITO/PPV and Ca/PPV interfaces are too small to play any significant role in the conduction properties of the device. In order to estimate the effect of an injection barrier ϕ_b on the $J-V$ characteristics we compare the injection and bulk limited current of a PPV device without traps. Well-known mechanisms for injection of charge carriers across an interface barrier are thermionic emission and Fowler–Nordheim tunneling. For current injection into low-mobility semiconductors as PPV, where diffusion effects must be taken into account, the thermionic emission-diffusion theory of Crowell and Sze[11] gives:

$$J=qN_c\mu F(0)\exp\left(-\frac{q\phi_b}{kT}\right),\qquad (5)$$

with $F(0)$ the electric field at the contact. The barrier height ϕ_b is lowered by the image force effect as:

$$\phi_b=\phi_{b0}-\Delta\phi=\phi_{b0}-\sqrt{\frac{qF(0)}{4\pi\epsilon_0\epsilon_r}}.\qquad (6)$$

For a given current density J, Eqs. (5) and (6) directly provide the boundary condition for the electric field $F(0)$ at the injecting contact. When the space charge in the bulk of the sample is also included, the dependence of the electric field on the position x (between 0 and L) is given by:[12]

$$F(x)=\sqrt{F(0)^2+\frac{2Jx}{\epsilon_0\epsilon_r\mu}}.\qquad (7)$$

By integration over x, the $J-V$ characteristic can be obtained for arbitrary ϕ_{b0}. In Fig. 4, J is plotted against V (solid line) for a device with $L=100$ nm, $\mu=10^{-6}$ cm^2/V s, $\phi_{b0}=0.35$ V, and $\epsilon_r=3$. For comparison, the limiting cases for an Ohmic contact [$F(0)=0$], implying SCLC according to Eq. (1), and diffusion-limited injection, Eqs. (5) and (6) with $F(x)=F(0)=V/L$, are also given. At low bias ($V<5$ V) the

calculated current is approximately equal to the diffusion-limited injection current, and at high bias ($V>15$ V) the current approaches the bulk SCLC current. Also plotted in Fig. 4 is the result for Fowler–Nordheim tunneling[4] with $F(0)=V/L$. It is clear that at low bias this injection mechanism is negligible with regard to diffusion-limited injection, whereas at high bias space-charge effects dominate the conduction. In general, it will depend on both ϕ_{b0} and L whether the conduction is injection or space-charge limited. We find that for $\phi_{b0}<0.2$ V the $J-V$ characteristics are given by Eq. (1) in the whole bias regime. Thus we estimate that the SCLC observed in all our hole-only devices arises from the fact that the injection barrier at the ITO-PPV interface is <0.2 V.

The results obtained in this study enable us to further investigate the relevance of the unbalanced electron and hole transport to the device efficiency of a polymer LED. As a consequence we have demonstrated that the presence of electron traps gives rise to a bias dependent efficiency.[13] At low bias the injected electrons are trapped and do not contribute to the radiative recombination process. With increasing bias the traps are filled, giving rise to a strong increase of the number of free electrons, which participate in recombination, and hence it increases the device efficiency.

In conclusion, we have demonstrated that the electron and hole currents in PPV devices with low contact barriers are determined by the bulk conduction properties of the polymer, and not by the injection properties of the contacts. The hole transport is well described by space-charged limited current with a hole mobility of 0.5×10^{-6} cm^2/V s. The electron transport is limited by traps which are exponentially distributed in energy with a density of 10^{18} cm^{-3}.

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