Temperature dependence of the charge injection in poly-dialkoxy-
-p-phenylene vinylene

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The injection of holes from a Ag electrode into poly-dialkoxy-p-phenylene vinylene is investigated by measuring the current–voltage characteristics as a function of temperature. For this model system, the hole injection is hindered by a contact energy barrier of about 1.0 eV. The observed temperature dependence of the injection-limited current does not agree with the predictions of classical injection models. A recent model, in which the spread in the charge transporting site energy due to disorder is taken into account, consistently describes the measured field and temperature dependence of the injection process. © 2001 American Institute of Physics.

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Since the discovery of polymeric light-emitting diodes, it has directly been recognized that charge injection is an important process with regard to their device performance. The charge injection process may be hindered by the presence of an interface barrier at either the electron or hole contact. Such interface barriers result in an unbalanced charge carrier injection, which gives rise to an excess of one carrier type and, consequently, in a large decrease of the conversion efficiency. However, knowledge of the mechanisms of charge injection into conjugated polymers is not nearly as comprehensive as for inorganic semiconductors. The classical injection mechanism used to describe charge injection is thermionic emission, which results in a current density J given by

$$J = A^* T^2 \exp \left( -\frac{q \phi_b}{kT} \right),$$

(1)

with $A^*$ the effective Richardson constant, $T$ the temperature, and $\phi_b$ the effective barrier, due to the offset in energy levels at the interface. Furthermore, at sufficient high fields, tunneling from the contact will become important due to strong band bending.

It has been pointed out that the thermionic emission model is not applicable to low mobility semiconductors because backflow will occur due to the large concentration of charge carriers at the interface. In that case, the diffusion-limited injection current is predicted to follow

$$J = qN_v \mu(T) E \exp \left( -\frac{q \phi_b}{kT} \right),$$

(2)

with $\mu$ the charge carrier mobility, $N_v$ the effective density of states in the semiconductor, and $E$ the applied electric field. The same result has also been obtained in the case of insulators at low or moderate fields, where space-charge effects are unimportant. It should be noted that in both thermionic emission (high mobility) and diffusion-limited injection (low mobility), the barrier height $\phi_b$ plays a dominant role in the injection-limited current (ILC).

As an alternative to the above-mentioned classical injection models, a model based on thermally assisted tunneling of carriers from the contact into localized states of the polymer has been formulated. This model has been further investigated by including energetic disorder and the image force effect in Monte Carlo (MC) simulations. These simulations indicate that in conjugated polymers an increase of $J$ with $V$ is due to the field dependence of the mobility and to an additional increase of the carrier density at the contact caused by the image force. Moreover, analytical treatment investigates explicitly the injection process by a first jump from the contact level into a random hopping system, followed by either a diffusive escape from the interface or a backflow to the electrode. This approach has been confirmed by MC simulation that shows that the primary injection event is essential and determines the temperature and field dependence of the injection process. In the polymer the density of transport states (DOS) can be described by a Gaussian distribution characterized by an energy width $\sigma$. The ILC is then given by

$$J \approx \int_a^{\infty} dx \ exp(-2\gamma x) w_{esc}(x) \int_{-\infty}^{\infty} dE \ Bol(E) g[U(x) - E],$$

(3)

with $\exp(-2\gamma x_0)$ the tunneling probability, $\gamma$ the inverse localization radius, and $U$ the electrostatic potential. Furthermore, $w_{esc}$ is the probability for a carrier to avoid surface recombination and the Boltzmann function $Bol(E)$ gives the occupation statistics. In this model the ILC [Eq. (3)] is determined by four parameters; the energy width $\sigma$, the dielectric constant $\varepsilon$, the nearest-neighbor distance $a$, and $\phi_b$, the energy distance from the electrode level to the center of the Gaussian DOS of the polymer.

In order to discriminate between the injection models based on backflow of carriers and models based on hop-
ping injection into a disordered organic conductor,\textsuperscript{7–11} we have investigated the temperature dependence of contact-limited currents in poly(p-phenylene vinylene) (PPV). For our dialkoxy-PPV (OC\textsubscript{10}C\textsubscript{10}−PPV), the hole mobility typically amounts to $\mu = 5 \times 10^{-7} \text{ cm}^2 / \text{V s}$,\textsuperscript{12} and the injection process is expected to be completely diffusion limited [Eq. (2)], with a temperature dependence $\mu(T) \exp(-q \phi_0 / kT)$. At low fields the mobility of OC\textsubscript{10}C\textsubscript{10}−PPV is characterized by $\mu(T) = \mu_{\infty} \exp(\Delta/kT)$, with $\Delta = 0.48 \text{ eV}$. In the present study silver (Ag) is used as an electrode, since noble metals form abrupt unreacted interfaces with the polymer.\textsuperscript{14} Furthermore, contrary to other noble metals, hole injection from silver (Ag) into PPV is hindered by an energy barrier ($\phi_0 \approx 1 \text{ eV}$),\textsuperscript{15} which is considerably larger than the activation energy ($\Delta = 0.48 \text{ eV}$) for conduction. From Eq. (2) it is therefore expected that the temperature dependence of the ILC is significantly stronger than of the space-charge-limited current (SCLC). From the temperature dependence of the current density–voltage ($J$–$V$) characteristics only a weak thermal activation of the ILC is observed, and the predicted $\exp(-\phi_0 / kT)$ behavior is completely absent. However, the hopping-based models\textsuperscript{7–11} consistently describe this strongly reduced temperature dependence of the injection process.

The devices that we have studied consist of a single OC\textsubscript{10}C\textsubscript{10}−PPV polymer layer sandwiched between two electrodes on top of a glass substrate. The polymer is spin coated on top of a patterned indium–tin–oxide (ITO) bottom electrode. The work function of ITO lies close to the valence band of PPV, resulting in an Ohmic contact.\textsuperscript{16} As a result, the hole injection into PPV from the ITO contact gives rise to a space-charge-limited current, which enables the determination of the hole mobility.\textsuperscript{16} The hole mobility as determined from the SCLC has been confirmed by field-effect measurements,\textsuperscript{12} transient electroluminescence,\textsuperscript{12} and by admittance spectroscopy.\textsuperscript{17} As a top electrode evaporated Ag is used. In Fig. 1 the $J$–$V$ characteristics for both hole injection from the ITO contact and the Ag contact are shown. As expected, it is found that the current for hole injection from the ITO contact behaves as a bulk-limited SCLC. This current is also found to be several orders of magnitude larger than the observed current for hole injection from the Ag electrode. This is a direct proof of the fact that the current for the case of injection from Ag is indeed injection limited.

An extrinsic process that would strongly affect the injection efficiency is the creation of interface states as a result of the evaporation of Ag. Such interface states could assist in the injection process and, therefore, mask the intrinsic injection properties. It has been reported by Ioannidis et al.\textsuperscript{18} that after evaporation of Au on a molecularly doped polymer the injection efficiency strongly increases in time due to relaxation of the interface. In order to exclude this kind of extrinsic injection process we have fabricated test devices, as indicated in the inset of Fig. 2. In these test devices the bottom ITO contact is covered by an additional layer of Ag that is evaporated before depositing the polymer layer and, therefore, cannot damage the polymer surface due to, for example, heat transfer during the evaporation process.

In Fig. 2, a $J$–$V$ plot for such a test device at $T = 300 \text{ K}$ is represented. Since the experimental hole injection curves for both the Ag bottom (positive voltage) and top contact (negative voltage) show identical behavior, it is demonstrated that the injection characteristics of the Ag–PPV contact is not affected by the deposition process. From the $J$–$V$ characteristics in Fig. 1 at $T = 300 \text{ K}$ and $T = 195 \text{ K}$ it is evident that the SCLC bulk current of the ITO contact exhibits a stronger temperature dependence (indicated by arrows) as compared to the ILC of the Ag contact. In Fig. 3 the normalized hole current injected from an ITO/Ag contact in an ITO/Ag/PPV/Ag device is shown as a function of temperature at low electric field ($5 \times 10^7 \text{ V/m}$). Also, the normalized temperature dependence of the SCLC hole current, governed by $\Delta$, is plotted together with the predicted activation energy $E_{\text{act}} = \phi_b + \Delta$ of Eq. (2). It appears from Fig. 3 that the thermal dependence of the ILC is not only far less than $E_{\text{act}} = \phi_b + \Delta$ ($\approx 1.5 \text{ eV}$), but even weaker than the thermal activation $\Delta (0.48 \text{ eV})$ of the mobility. This strongly reduced temperature dependence of the ILC compared to the SCLC is in total disagreement with the classical model [Eq. (2)].

In order to test the applicability of the hopping-based models,\textsuperscript{7–11} we have compared our experimental data with Eq. (3). From the field and temperature dependence of the hole mobility of our OC\textsubscript{10}C\textsubscript{10}−PPV, $\alpha = 0.11 \text{ eV}$ and $\sigma = (1.2 \pm 0.1) \text{ nm}$ have been extracted.\textsuperscript{19} Furthermore, from impedance measurements $\varepsilon = 2.1$ has been found.\textsuperscript{17} As a re-

\[J = \frac{q \mu \varepsilon}{kT} \exp\left(-\frac{\phi_b}{kT}\right) \exp\left(-\frac{\sigma}{\sqrt{kT}}\right)\]
result, all four parameters are fixed. The temperature dependence of the ILC as calculated from the hopping model [Eq. (3)] with a 0.95 eV barrier height as plotted in Fig. 3. It is demonstrated that the weak temperature dependence of the experimental ILC is excellently reproduced by the predictions of the hopping model.

In a Gaussian density of states the equilibrium energy, to which the charge carriers have to be injected, is located at an energy $\sigma^2/kT$ from the center of the Gaussian DOS. As a result, the injection barrier decreases with decreasing temperature, leading to a much weaker temperature dependence of the ILC as compared to $\exp(-\phi_b/kT)$. The experimental results in this article confirm these predictions. In Fig. 4 the injection-limited hole current from the Ag contact is shown at an electric field of 5 \times 10^7 V/m. The solid line is calculated from a random hopping model [Eq. (3)] with $\phi_b=0.95$ eV for Ag and $\phi_b=1.05$ eV for Al. The dashed line represents a current activated by the mobility with $\Delta=0.48$ eV. The dotted line represents diffusion-limited injection [Eq. (2)] with an activation energy $E_{act}=\phi_b+\Delta=1.43$ eV.

In conclusion, injection-limited hole currents from Ag and Al into PPV exhibit a very weak temperature dependence, in spite of the presence of a large injection barrier energy of 1 eV. Such a behavior is in contradiction with classical thermionic injection models in which the temperature dependence of the injection process is dominated by the injection barrier. The reduced temperature dependence of the ILC is explained by a model which is based on thermally assisted hopping from the electrode into the localized states of the PPV, which are broadened due to disorder.