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Performance of Injection-Limited Polymer Light-Emitting Diodes

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ABSTRACT.

The electro-optical characteristics of a polymer light emitting diode (PLED) with a strongly reduced hole injection have been investigated. The device consists of a poly-*p*-phenylene vinylene semiconductor with a Ag hole injecting contact, which has an injection barrier of about 1 eV. It is observed that the light and current density of such an injection-limited PLED strongly exceed the expected device characteristics. Numerical calculations of the injection-limited PLED show that the enhanced performance can be explained by a very high electric field at the hole injecting contact, due to trapped electrons.

INTRODUCTION

Directly after the discovery of polymer light emitting diodes (PLEDs) [1], charge injection has been recognized as an important process for the performance of a PLED [2]. However, the mechanisms of charge injection into conjugated polymers are poorly understood, compared with the knowledge of inorganic semiconductors. Contrary to inorganic semiconductors like Si, the charge transport in conjugated polymers is determined by tightly bound charge carriers on transporting sites that are subject to disorder both energetically and spatially [3]. Consequently, the nature of the charge injection from a metallic contact into the conjugated polymer will differ notably from mechanisms like thermionic emission and Fowler-Nordheim tunneling. These mechamisms are normally used to describe injection in crystalline semiconductors with well-defined transport levels of the delocalized charge carriers.

To account for nature of transport in conjugated polymers, a model based on thermally assisted tunneling of carriers from the contact into localized states of the polymer has been formulated [4]. This model has been further investigated by including energetic disorder and the image force effect in Monte Carlo (MC) simulations [5,6]. 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 [6]. 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 [7]. 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 [8].

Recently, it has been demonstrated that the hole injection from a Ag blocking contact into poly-*p*-phenylene vinylene (PPV) is excellently described by the hopping based injection model [9]. It has been shown that the temperature dependence of the injection-limited current is much smaller than is expected from classical thermionic emission. This is caused by the broad distribution of energies of the transport sites in the polymer resulting in an injection into tail states of the distribution. Therefore, the energy a carrier needs in order to hop from the electrode into the transport level of the polymer is strongly reduced.

INCORPORATION OF THE INJECTION-LIMITED HOLE CONTACT IN A PLED

Charge injection is an important process with regard to the performance of PLEDs. Especially for materials with a large energy gap, as applied for blue PLEDs, large energy barriers at the injecting interface are expected. So far, only experimental results on PLEDs with Ohmic electron- and hole contacts have been modeled [10]. By incorporating the injection model based on thermally assisted hopping into the PLED device model also PLEDs with strongly hindered hole injection can be investigated. The result of the hole injection can be incorporated into a device model in order to calculate the device current with a limited hole injection. The current for strong electric fields, when the diffusion is negligible is the sum of the electron and hole current:

$$J = J_p + J_n = em_p\, pE + em_n\, nE \qquad (1)$$

with E the electric field, p and n respectively the hole and electron concentration and m_p , m_n the hole and electron mobility. The electric field throughout the device is calculated by the Poisson equation:

$$\frac{e_0 e_r}{e}\frac{dE}{dx} = p - n - n_t \qquad (2)$$

Where e_0 the permittivity of vacuum, e_r the relative dielectric constant, and n_t the concentration of trapped electrons. For the material under consideration, dialkoxy-PPV (OC_1C_{10}-PPV), the hole mobility is given by [11]:

$$m_p(E) = m_p(0)\exp(g\ddot{O}E) \qquad (3)$$

With $m_p(0)$ the mobility at zero field. The hole mobility m_p of OC_1C_{10}-PPV is characterized by a zero field mobility $m_p(0) = 5\times10^{-11}$ m^2/Vs and a field parameter $g = 5.4\times10^{-4}$ $(m/V)^{(1/2)}$ [11]. The bulk limited electron current is a few orders of magnitude lower than the hole current [12,13] and can be described by a lower electron mobility [12], or by a trap limited electron current, with the transport parameters of the hole mobility, together with an electron trap [13].
Combining the results of the electron- and hole transport a device model for PLEDs has been proposed in which the recombination of electrons and holes is of the Langevin-type, in which the rate-limiting step is the diffusion of electrons and holes toward each other [10]. The continuity equation then gives:

$$\frac{1}{e}\frac{dJ_n}{dx} = -\frac{1}{e}\frac{dJ_p}{dx} = Bp(x)n(x) \qquad (4)$$

With B the recombination constant, determined by Langevin recombination [10]. The light output of the device is proportional to the total number of recombination, reduced by the non-

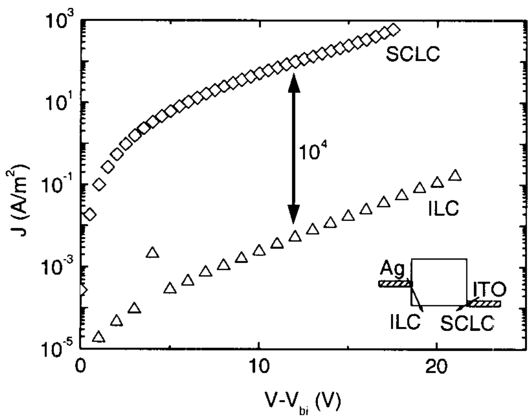

Figure 1. Hole current density J versus voltage V at room temperature of an ITO/PPV/Ag hole-only device with thickness L = 240 nm. For hole injection from ITO the current is space-charge limited (SCLC), for hole injection from Ag the current is injection-limited (ILC). The calculated SCLC has been plotted as solid lines.

radiative recombination as a result of the spin statistics and non-radiative recombination centers and further reduced by the losses in the device.

EXPERIMENT

The injection-limited PLED devices that have been investigated consist of OC_1C_{10}-PPV sandwiched between two electrodes on top of a glass substrate. The OC_1C_{10}-PPV polymer is spin-coated on top of a silver (Ag) bottom electrode and is covered by a Ca contact. The Ca top electrode has a work-function which is close to the conduction band energy of OC_1C_{10}-PPV [14], resulting in a Ohmic contact for the electron injection[13]. The Ag-contact at the other hand, makes an injection barrier of 1 eV with the valence band of the PPV [14]. As a result, the hole injection into PPV from the Ag contact is strongly hindered. Furthermore, for comparison also bulk-limited PLED devices have been made, where the OC_1C_{10}-PPV has been spin-coated on top of an ITO contact.

As the device current of a PLED based on PPV is hole dominated [13], it is expected that a reduction of the hole current by a high hole contact barrier will strongly reduce the device current. In figure 1 it is demonstrated that for hole injection from Ag the hole current is reduced by 4 orders of magnitude as compared to the bulk space-charge limited hole current. As a result the number of holes in the injection-limited PLED (IL-PLED) is also reduced by a factor 10^4. The current-density voltage (J-V) characteristics for both the IL-LED and the PLED are shown in figure 2, measured at room temperature. It is observed that the current-density of the IL-LED is, as expected, strongly reduced compared with the current density of the PLED. Due to the 10^4 reduction in hole density it is expected that the current of the IL-PLED will behave as a space-charge limited electron-only device. From figure 2 it is observed that the IL-LED indeed follows the electron-only current at low voltages. However, at an applied bias V of typically 7 V, the current starts to increase rapidly from the electron current.

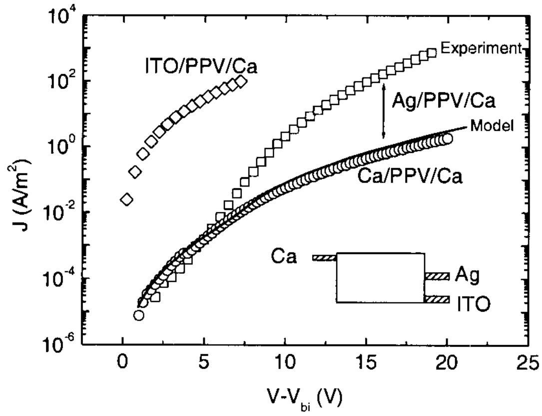

Figure 2. Current density *J* versus voltage *V* at room temperature for an ITO/PPV/Ca polymer light emitting diode (PLED), a Ag/PPV/Ca injection-limited PLED (IL-PLED) and a Ca/PPV/Ca electron-only device, all with thickness L = 240 nm. Also shown is the numerically calculated *J-V* characteristic for the IL-PLED, using a barrier height j_b=0.95 eV for the hole injection.

ENHANCEMENT OF THE HOLE INJECTION

The characteristics of a double carrier device have been described by a device model based on the current density equation (equation 1) together with the Poisson equation (equation 2) and the continuity equation (equation 4). Incorporation of the field and temperature dependence of the injection current into the device model gives the characteristics for a high hole injection barrier. The result is also shown in figure 2. It is observed that the device current as obtained from the device model is comparable with the electron-only current, even for high bias. When the hole injection is negligible, the electron space charge from the Ca contact is not compensated and consequently the space-charge limited electron current is the maximum possible current in the PLED. As a result, the observed increase for V>7 V must originate from an enhanced hole injection. As the hole injection strongly increases with increasing field, the origin of the enhanced hole injection will be a enlarged electric field at the interface.

A possible origin of an enhanced electric field at the hole-injecting contact might be tunneling through an interface barrier or the trapping of electrons at the interface, as schematically indicated in figure 3. Enhancement of charge injection by a tunnel barrier has recently been demonstrated by Murata et al. [15]. Such a tunnel barrier will prevent the electrons to flow into the hole injection contact. Consequently, a large electric field across the tunnel barrier builds up, which gives rise to an increased hole injection. However, the presence of such an electron-blocking tunnel barrier is not in agreement with the fact that we observe the bulk-limited electron current at low voltages in our IL-PLEDs. An alternative explanation is the presence of electron traps at the Ag/PPV interface, characterized by an extension length of the traps from the contact into the device. Such a non-uniform spatial trap distribution is also used e.g. by Hwang and Kao [16] to explain the field and thickness dependence of an organic

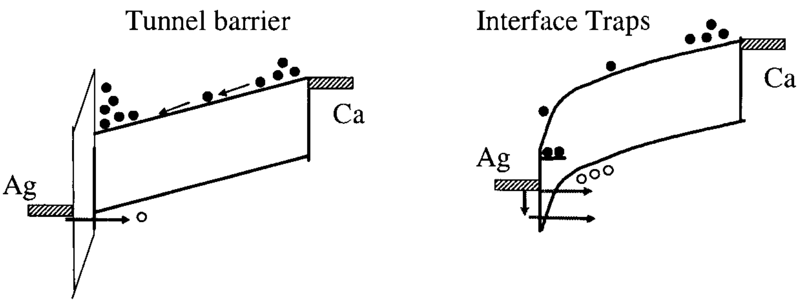

Figure 3. Possible origin of the enhanced hole injection: a) electron blocking barrier at the hole contact, b) small interfacial region with electron traps near the hole contact. In case (a) the hole tunneling through the barrier is enhanced by strong band banding of the tunnel barrier, in case (b) the hole injection is increased by the extra lowering of the effective barrier.

semiconductor sandwiched between two metal contacts, assuming a trap near the metal contacts. The traps may be attributed to process conditions or misfit of the lattices. For the injection-limited PLED, the electron trap near the contact will increase the electric field at the Ag/PPV interface, leading to an enhanced hole injection. Furthermore, in a hole-only device, as is used in our study of hole injection from Ag into PPV (figure 1), these electron traps remain unfilled and therefore do not play a role. Due to the small space charge in such a hole-only device, the electric field is determined by the potential difference at the contacts, which directly gives the relation between electric field and injection-limited current.

ELECTRON TRAPS AT HOLE CONTACT

In order to model the influence of electron interface traps we incorporate in our model a small interfacial region of a few nm which contains interface traps. In this region the relation between trapped electrons n_t and free electrons n is given by

$$n_t = \frac{n}{q} \tag{5}$$

As a result we have added one additional parameter q to our PLED device model. In figure 4a the calculated *J-V* characteristics are shown for q=5x10^{-5}. The calculated *J-V* characteristics consistently describe the experimental results of the IL-PLED. Furthermore, in figure 4b the light-output is shown, demonstrating the same increase of light output at high applied bias as is observed for the current. This is a very clear indication of the enhanced hole injection, as the light output is proportional to the recombination rate, which is given by the product of holes and electrons (equation 4). It can be seen from figure 4b that inclusion of an interface trap also gives good agreement between model and experimentally observed light output.

The calculated electric field at the hole injecting contact (Ag-PPV), resulting from the electron space charge, is shown in figure 5. This graph demonstrates the influence of inclusion of an electron trap near the hole injecting interface. For a current above J = 0.01 A/m^2, the resulting electric field at the Ag-PPV contact starts two grow rapidly for a device with interface traps.

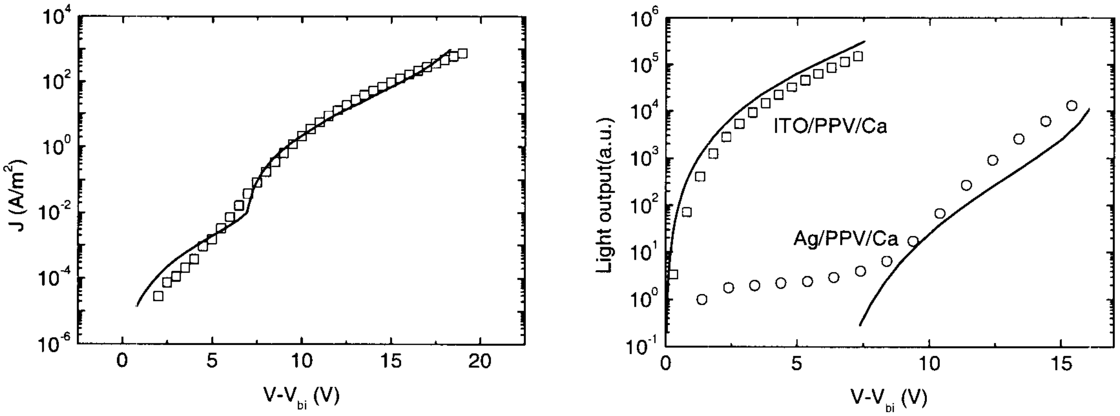

Figure 4. a) Current density *J* versus voltage *V* at room temperature for the Ag/PPV/Ca injection-limited PLED (IL-PLED). The calculated current is plotted as a line for such a device. The calculation includes an electron trap in a small interfacial region near the hole contact, with a ratio *q* between free and trapped electrons, $q = 5x10^{-5}$. b) Light output of both the ITO/PPV/Ca (PLED) and the Ag/PPV/Ca (IL-PLED) device at room temperature, together with the calculated light output from the device model incorporating an electron trap near the hole contact, plotted as a line.

The hole injection, which is strongly field dependent is therefore enhanced by several orders of magnitude, compared with the hole injection from a contact with no electron traps. For high enough trap concentration, the electron space charge as generated by the current results in a large interface field, and as a result the hole injection current is even dominant.

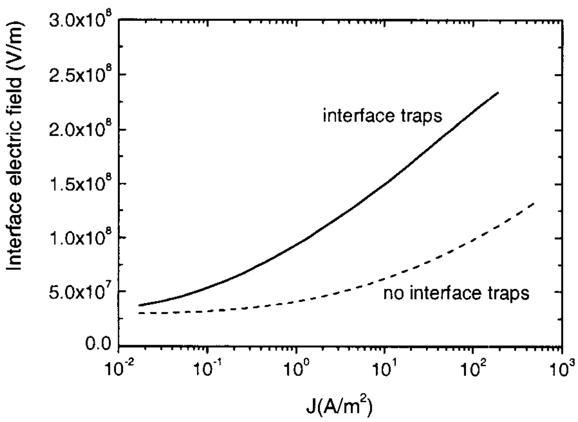

Figure 5. Electric field at the hole injecting contact as a function of applied current through the device. The dashed line represents the interface field for a device without interface traps, the solid line for inclusion of interface traps with $q = 5x10^{-5}$.

A clear illustration of the enhanced hole injection is found in figure 6a, where the average hole and electron concentration are plotted as a function of voltage for both a device without traps and one including electron traps near the hole injecting contact. It is directly observed that the contribution of holes is enhanced for higher applied bias by several orders of magnitude by the presence of interface traps. As the holes also have a higher mobility, the device current for high bias is completely determined by the hole injection current. In figure 6b the potential as a function of distance near the Ag hole injecting contact is plotted. This plot is obtained by integrating the electric field from the hole contact barrier, and taking into account the potential energy lowering due to the image force effect. This image force induced potential lowering is also taken into account in the hopping based injection model that is used in the device model as the boundary condition for hole injection, and is an important reason for the increase of hole injection current as is illustrated in figure 6b. The image force causes a lowering of the potential barrier thereby enhancing the hopping rate of charge carriers from the Ag contact into the polymer.

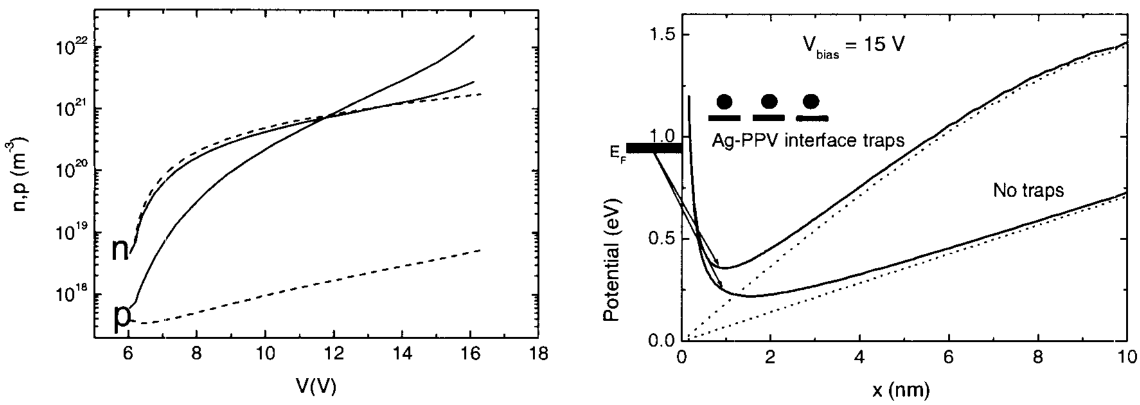

Figure 6. a) Mean concentration of electrons *n* and holes *p* as a function of applied voltage for an IL-LED, calculated for a device with no interface trap (dashed lines) and with an interface trap with $q = 5x10^{-5}$. b) Electrostatic potential as a function of distance for an applied bias of 15V. The arrows indicate the jump to a nearest neighbour distance in the polymer, which is the most probable first hop the injected carriers will make.

CONCLUSIONS

In conclusion, it is found that the injection-limited hole current in a polymeric LED is significantly enhanced by the presence of electrons. The increase of the hole current is quantitatively explained by an electron trap near the PPV interface, which enlarges the electric field at the interface resulting in a strong enhancement of the hole injection.

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