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Electro-optical properties of a polymer light-emitting diode with an injection-limited hole contact

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The electro-optical characteristics of a polymer light-emitting diode with a strongly reduced hole injection have been investigated. A silver contact on poly-dialkoxy-*p*-phenylene vinylene decreases the hole injection by five orders of magnitude, resulting in both a highly reduced light output and current. However, at high applied voltages, the current and light output strongly exceed the predictions based on the reduced hole injection, which is explained by an enhanced electric field near the hole-injection contact due to trapped electrons. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1543255]

Soon after the discovery[1] of the polymeric light-emitting diode (PLED), it was realized[2] that charge injection in a polymeric semiconductor is an important process with regard to device performance. A high energy barrier at one of the contacts gives rise to an unbalanced charge carrier injection, which strongly reduces the conversion efficiency of current into light. Experimentally, it has been demonstrated that the performance of PLEDs based on the conjugated polymer dialkoxy poly-phenylene vinylene (OC_1C_{10}-PPV) is not limited by injection.[3] The matching of the work functions of indium tin oxide (ITO) and calcium with the valence and conduction band of OC_1C_{10}-PPV, respectively, gives rise to efficient charge injection. Experiments on PPV-based PLEDs have been consistently described by a device model with ohmic contacts for both hole and electron injection.[4] For green and blue PLEDs, contact barriers will naturally appear due to their large band gap. Clearly, for the electro-optical characterization of these large band gap PLEDs, a device model has to be developed that incorporates the presence of large contact barriers.

As a first attempt, contact barriers have been incorporated in PLED device models by using the classical, diffusion-limited, thermionic emission model.[5,6] In a recent experimental study, however, it has been demonstrated that hole currents from silver and aluminum into OC_1C_{10}-PPV exhibit a very weak temperature dependence, in spite of the presence of a large injection barrier of 1 eV.[7] This behavior is in contrast with the thermionic emission model which predicts a strong thermal activation, dominated by the large injection barrier. The field and temperature dependence of the injection-limited (IL) current is consistently explained by an injection model based on injection into tail states of the energetic distribution of hopping sites.[8]

In this letter, the role of an injection barrier on the performance of a PLED is investigated by incorporating the hopping-based injection mechanism in the device model. The current and light output of an IL PLED have experimentally been investigated for a PPV-based PLED with limited hole injection from a Ag anode. Since the field and temperature dependence of the hole injection from the Ag contact into the PPV is known,[7] the current and light output of this IL PLED can be predicted from the PLED device model. It is expected from these calculations that the current and light output of the device will be strongly reduced due to the hindered hole injection from the Ag contact. At low voltage, the expected reduction of the current and light output due to the presence of the hole contact barrier is indeed observed. However, at higher bias (>7 V) the experimental light and current density exhibit a strong increase, which is attributed to an enhanced electric field at the injection-limited hole contact due to trapped electrons.

In order to clarify the effect of a contact barrier on PLED performance, four different types of devices have been investigated, all consisting of a spin coated layer of the polymer OC_1C_{10}-PPV sandwiched between two electrodes. As a reference, an ITO/OC_1C_{10}-PPV/Ca PLED with two ohmic contacts was made.[4] An injection-limited ITO/Ag/OC_1C_{10}-PPV/Ca PLED (IL PLED) was then constructed, in which the ITO bottom contact has been covered by Ag. For the investigation of reduced hole injection from the Ag electrode, ITO/Ag/PPV/Ag devices were constructed[7] with an electron-blocking Ag top contact. In order to discriminate whether the current in the IL PLED is dominated by the (reduced) hole or the electron current, Yb/PPV/Ca electron-only devices were investigated as well.

Figure 1(a) shows the current-density–voltage (J–V) plot for the ITO/Ag/PPV/Ca IL PLED, together with the electron-only Yb/PPV/Ca and the ITO/Ag/PPV/Ag devices. It is demonstrated that the hole current injected from a Ag contact is about one order of magnitude smaller than the bulk-limited electron current. As a result, the current of the IL PLED is expected to be identical to the electron current, which is verified by the calculations using the PLED device model including hopping-based injection (solid line). Experimentally, it is observed [Fig. 1(a)] that, for low bias, the J–V

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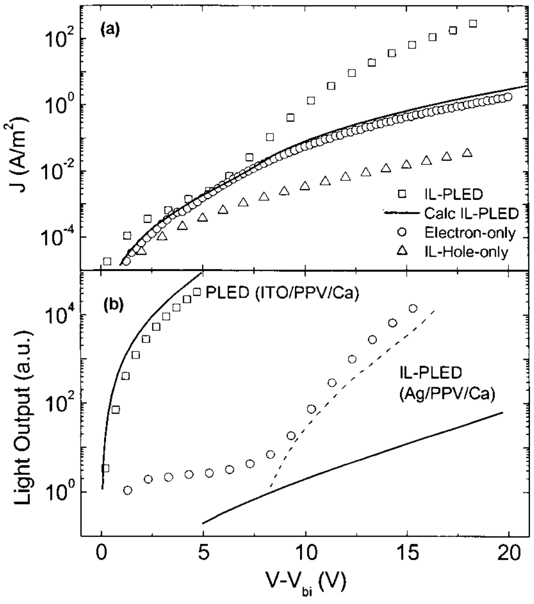

FIG. 1. (a) $J-V$ at room temperature for a Ag/PPV/Ca IL PLED. For comparison, an ITO/Ag/PPV/Ag IL hole-only device and an Yb/PPV/Ca electron-only device are also shown, all with film thickness $L=240$ nm. The solid line represents the numerically calculated $J-V$ characteristic of the IL PLED for a hole injection barrier $\phi_B=0.95$ eV. (b) Light output of the ITO/PPV/Ca (PLED) and the Ag/PPV/Ca (IL PLED) device at room temperature. The solid lines represent the calculated light output without interface traps, the dashed line shows the light output of the IL PLED with traps at the Ag contact.

characteristics of the ITO/Ag/PPV/Ca IL PLED are indeed identical with the electron-only characteristics. However, at an applied bias of typically $V=7$ V, the current starts to depart from the expected electron current. Since the space-charge limited electron current shown in Fig. 1(a) is the maximum current an electron-only device can contain, the increase of the IL PLED must arise from an increased hole injection. This is confirmed by the observed light output of the IL PLED, as shown in Fig. 1(b). The light output is proportional to the product of electron and hole density,[4] thus the reduced hole injection decreases the light output of the IL PLED compared with a bulk-limited PLED. It is observed from Fig. 1(b) that at low voltages, the light output of the IL PLED is indeed decreased by several orders of magnitude as compared to the ITO/PPV/Ca device. The difference between the calculated and measured light output is caused by the detection limit of the light sensor. The rapid increase of the light output above 7 V also points towards a large enhancement of the hole injection from the Ag contact into the polymer.

A possible explanation for the enhanced hole injection at high voltages is an interfacial layer at the Ag anode (see inset of Fig. 2) with electron traps. At sufficient voltages these traps become filled, and the trapped electrons will increase the electric field at the Ag/PPV interface, leading to an enhanced hole injection. It should be noted that such electron traps remain unfilled in an ITO/Ag/PPV/Ag hole-only device, and therefore do not play a role in the investigation of the injection-limited hole current.[7] We have incorporated electron traps in an interfacial layer extending a few nm from the contact. The effect of these traps is described by a single parameter θ that represents the ratio of free electrons n and trapped electrons n_t

$$\theta=\frac{n}{n+n_t}. \tag{1}$$

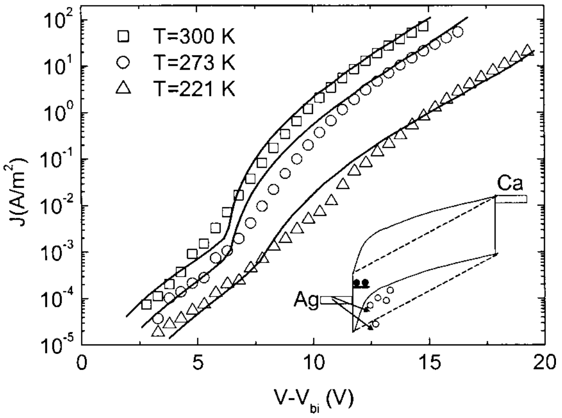

FIG. 2. $J-V$ of the IL PLED at different temperatures. The solid lines represent the calculated device current including electron traps in an interfacial layer of a few nanometers near the Ag contact. The inset shows a schematic potential distribution without (dashed line) and with (solid line) interface traps.

In Fig. 2, the temperature dependence of the $J-V$ characteristics of the ITO/Ag/PPV/Ca IL PLED is shown, together with the calculated current from the device model in which, next to hopping-based injection, interface traps have also been included. The only unknown parameter in the device model is the trap parameter θ [Eq. (1)]. It is demonstrated (Fig. 2) that the strong increase of the experimental current at high voltages is consistently described by introducing an interfacial layer of electron traps. The ratio θ found from the $J-V$ characteristics is plotted in Fig. 3 as function of temperature.

For a single-level shallow trap in a band-like semiconductor, the temperature dependence of the ratio θ is given by[9]

$$\theta=\frac{n}{n+n_t}=\frac{N_C}{N_t}\exp\left(-\frac{E_C-E_t}{kT}\right), \tag{2}$$

where N_C is the effective density of states of the band, N_t the number of trap sites, and E_C-E_t the trap depth. However,

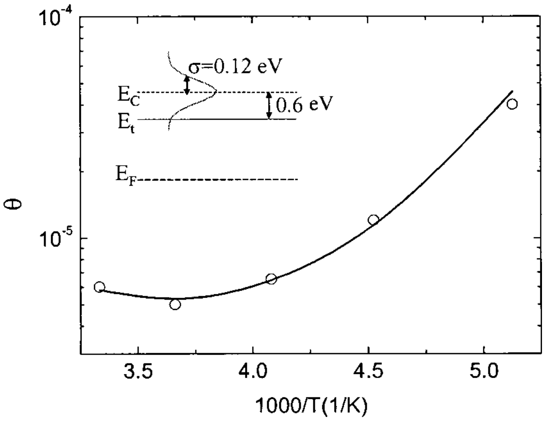

FIG. 3. Ratio θ of free and trapped electrons as a function of temperature. The solid line represents the temperature dependence for a Gaussian DOS with energy width $\sigma=0.12$ eV and a trap depth $E_C-E_t=0.6$ eV.

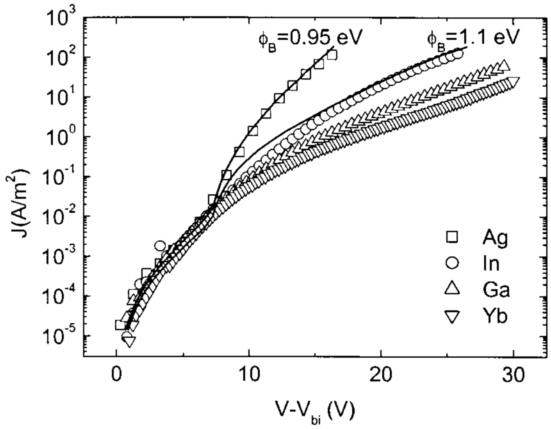

FIG. 4. IL PLED device current at room temperature for different contact materials as a function of applied voltage. Thickness of the devices is $L = 240$ nm. The solid lines represent the numerically calculated $J-V$ characteristics for barrier heights ϕ_B of 0.95 and 1.1 eV, respectively.

for strongly disordered semiconductors the transport sites have a Gaussian distribution of energies,[10] characterized by an energy width σ. From mobility measurements on OC_1C_{10}-PPV, a typical energy width of $\sigma = 0.11-0.12$ eV has been obtained.[11] In such a disordered system, the ratio θ between free and trapped carriers [Eq. (1)] in case of a shallow trap is then given by

$$\theta = \frac{N}{N_t}\exp\left[\frac{1}{2}\left(\frac{\sigma}{kT}\right)^2 - \frac{E_C - E_t}{kT}\right], \tag{3}$$

with N the number of transport sites. It is shown in Fig. 3 that the experimentally obtained θ is in agreement with Eq. (3) for a trap energy level $E_C - E_t = 0.6$ eV. Thus, the observed rise as well as the temperature dependence of the current of the IL PLED can be simultaneously explained by the presence of electron traps near the Ag contact. The trap concentration N_t in Eq. (3) has been found to be $N_t = 2 \times 10^{24}$ m^{-3} for an interfacial layer extending $d = 10$ nm into the polymer. For these parameters the calculated light output is also in good agreement with the experimentally obtained characteristics [Fig. 1(b)]. It should be noted that it is, not the concentration of electron traps N_t, but the total number of electron traps per area, $N_{it} = N_t d = 2 \times 10^{16}$ m^{-2}, that governs the $J-V$ characteristics. The increase of the electric field at the interface depends only weakly on the exact spatial distribution of the electron traps.

In order to investigate whether the enhanced hole injection at high fields occurs for electrodes other than Ag, IL PLEDs with indium and gallium anodes have also been investigated. From the work functions energy barriers around 1 eV are expected for both In and Ga, although the injection properties could be more complicated due to possible chemical reactions at the interface.[12] Figure 4 demonstrates that also for In and Ga, the current of the IL PLED starts to deviate from the electron-only current (Yb) at high fields, pointing to an enhancement of the hole injection. However, the enhancement of the current for Ga and In shows a weaker dependence on the applied bias as compared to Ag. As the injection current is very sensitive to the injection energy barrier, the device current of the IL PLED is also calculated for a barrier height of 1.1 eV, assuming the same concentration and depth of the interface traps. This calculated current density approaches the current of an IL PLED with an In anode, as shown in Fig. 4. In the low bias regime (<7 V) it is observed from Fig. 4 that the current of the IL PLEDs with Ga, In, and Ag fall on top of the electron-only (Yb) current. This behavior excludes an alternative explanation for the occurrence of enhanced hole injection in our devices, namely, the presence of an electron-tunneling barrier at the anode.[13] The fact that at low fields the current of the IL PLED is anode independent would imply that exactly the same tunneling barrier would be formed on the noble metal Ag as on the reactive Yb, which is highly unlikely.

In conclusion, it has been demonstrated that at low voltages, the characteristics of a PLED with a strongly hindered hole injection are governed by the transport properties of the electrons. The rise of the device current at high voltages, however, is caused by an enhancement of the hole injection. The field, temperature, and barrier-height dependence of the current of such an injection-limited PLED is consistently described by including an interfacial layer containing electron traps at the hole contact.

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