Symmetric light emitting devices from poly(*p*-di ethynylene phenylene) (*p*-di phenylene vinylene) derivatives

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Light emitting devices were fabricated from 2,5-dialkoxy derivatives of poly(*p*-di ethynylene phenylene-*p*-di phenylene vinylene) (PDEPDPV) sandwiched between indium tin oxide (ITO) and Al. The current–voltage (*I*–*V*) curve, electroluminescence (EL) intensity-voltage ($I_{\mathrm{EL}}-V$) curve, and the EL spectra were identical in forward and reverse bias. The $I-V$ curves were also symmetric under illumination, with $I\approx 0$ and $V=0$, suggesting a negligibly small internal electric field. At high bias voltage, carrier injection was found to be dominated by tunneling at the interfaces. At low bias voltage, tunneling among localized states at the Fermi level prevailed. The behavior is discussed in relation to Fermi-level pinning at defect states in the interfaces with the ITO and Al. © *1995 American Institute of Physics.*

Remarkable progress in developing π-conjugated polymer-based light emitting diodes (LEDs) has been achieved[1–6] since the discovery of electroluminescence (EL) in poly(*p*-phenylene vinylene) (PPV).[1] Considerable recent efforts to improve the devices by increasing the carrier injection at the electrodes[7] and by using multilayer structures to confine the electron and hole carriers have been reported.[8] The most common structure of these diodes is a sandwich geometry in which the polymer is spin coated onto an indium tin oxide (ITO) substrate and the top metal electrode is evaporated onto the emissive polymer layer. The current–voltage ($I-V$) behavior of these devices is usually similar to that of a conventional rectifying diode, in which a positive voltage applied to the ITO is the forward bias, and EL is observed only in this polarity.

In the present work we describe devices made of 2,5-dialkoxy derivatives of the novel polymer poly(*p*-di ethynylene phenylene-*p*-di phenylene vinylene) (PDEPDPV). Their properties differ substantially from the previously reported PPV-based LEDs, which displayed conventional rectifying $I-V$ characteristics. The PDEPDPV-based devices emit light of identical spectra for both polarities of the biasing voltage. We present the results of the electrical and optical characterization and discuss the physical phenomena that may be responsible for this unusual behavior.

The structure of PDEPDPV is shown in the inset of Fig. 1. It was synthesized in a Heck-type coupling from a substituted diethynyl arene reacting with a dibromoaryl compound in the presence of the catalylst $\mathrm{PdCl_2/CuAc_2/PPh_3}$ as described elsewhere.[9] ITO/PDEPDPV/Al devices were fabricated by spin coating Balzers or Standish LCD ITO-coated glass with a 6 mg/ml PDEPDPV solution in toluene or chloroform either in air or in a protective nitrogen atmosphere (oxygen and water levels of ~2 ppm). The Balzers silica glass plates were stripped of their ITO coating over roughly

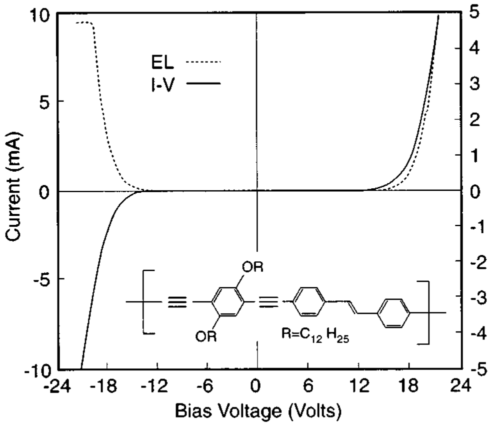

FIG. 1. A typical $I-V$ curve of a PDEPDPV device (solid line), and the dependence of the integrated intensity of the EL on the applied bias voltage (dotted line) at $T=77$ K. The inset shows the molecular structure of PDEPDPV.

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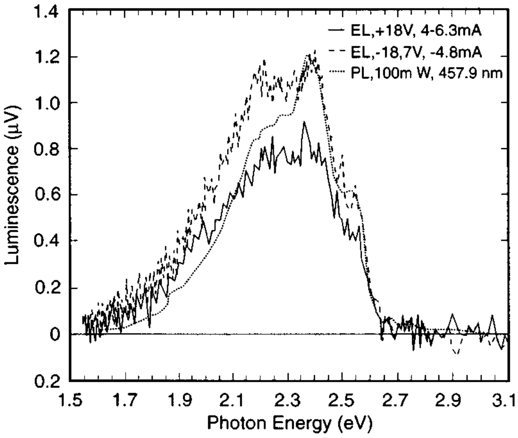

FIG. 2. EL spectra for positive and negative bias voltage of 18 V of a typical PDEPDPV device (solid lines) compared to the PL spectrum (dotted line) at $T=77$ K.

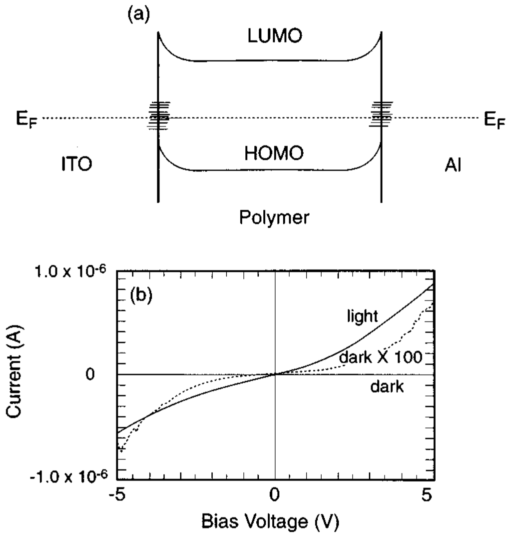

FIG. 3. (a) The suggested band diagram for PDEPDPV devices at $V=0$ resulting from a high density of deep interface states. (b) The photoresponse of a PDEPDPV device at saturation illumination at $T=300$ K. Note that the photocurrent is larger than the dark current by about two orders of magnitude, but it is still approximately zero at $V=0$.

one-third of the surface by dissolving the ITO in a standard aqua-regia solution; the Standish ITO was partially stripped by the manufacturer. The ITO was nominally 500 Å thick with a sheet resistance of ~200 Ω/square. The polymer solutions were pumped through 0.2 or 0.5 μm syringe filters into clean glassware for storage until use. The polymer layer had typical thicknesses of 1000–2000 Å. Al contacts with an area of ~10 mm^2 were thermally or *e*-beam evaporated onto the PDEPDPV layer in chambers with base pressures of $\sim 2\times 10^{-7}$ and $\sim 2\times 10^{-6}$ Torr, respectively.

$I-V$ measurements were performed with a Keithley 236 source-measure unit (SMU) interfaced to a PC; the SMU was used to bias the ITO layer positively or negatively with respect to the Al electrodes. Many of the measurements were performed with the devices submerged in liquid N_2 for heat-sinking purposes; their lifetime under these conditions was indefinite. Measurements at room temperature without addition of protective layers yielded lifetimes of up to several hours. The broadband EL and photoluminescence (PL) intensities (I_{EL} and I_{PL}, respectively) were measured by suspending a photomultiplier tube (PMT) directly above a lens in close proximity to the device. The EL and PL spectra were measured by directing the collected light from the device into a Jarrell–Ash monochromator with 7 nm resolution, followed by a Si photodiode.

Figure 1 presents a typical $I-V$ curve of a PDEPDPV device at 77 K. As clearly seen, it is symmetric in both forward and reverse bias voltages with a turn-on voltage of ~12 V. The $I_{EL}-V$ curve is also presented in Fig. 1. It closely follows the $I-V$ curve, and the device clearly emits symetrically with either polarity of the electrodes. The curves show an exponential behavior at $V\geqslant 6$ V similar to other reported LEDs (see below). We note that no significant changes were found in the $I-V$ curves upon cooling from 300 to 77 K. In addition, the curves are similar to those of forward biased ITO/PPV/Al LEDs, suggesting a quantum efficiency of ~0.05%.

In order to study the nature of the reverse bias emission, the EL spectra were measured in both biasing directions under identical values of V and I and are shown in Fig. 2. The spectra are identical and very similar to the PL, which is also shown in Fig. 2. This similarity shows that the mechanism leading to emission in both biasing directions is identical and probably due to exciton recombination. This is particularly significant for the reverse bias spectrum, where avalanche emission could otherwise be suspected. The coincidence of the EL and PL is also similar to that observed in PPV-based devices[6,10] and distinct from that of poly(*p*-phenylene ethynylene) (PPE)-based emitters.[6,10,11] On the other hand, the weak vibronic structure of the emission is similar to that of PPE films and devices and distinct from the PPVs, where it is very pronounced.

In PPV based LEDs, the $I-V$ characteristics of diodes prepared with different metal electrodes have indicated that the metal and ITO work functions determine the barrier heights for electron and hole injection, respectively, at their interfaces with the polymer.[12] This picture is invalid in the present case of PDEPDPV-based structures: Whereas the work functions of Al and ITO, 4.3 and 4.8 eV, respectively, significantly differ, the $I-V$ and $I_{EL}-V$ curves are symmetric. This behavior is consistent with Fermi energy (E_F) pinning by a high density of deep defect states at the interfaces. These defects can capture carriers from the bulk, creating barriers at the interfaces. The band diagram describing this situation is illustrated in Fig. 3(a). Whereas contact of a clean surface with a metal usually results in charge exchange between the metal and the surface states, in the case of a high density of surface states the barrier height at the interface is not effected by the presence of the metal, resulting in pinning of E_F at the defect states.

As Fig. 3(a) clearly shows, pinning of E_F close to the interface results in a negligibly small internal electric field E_F in the polymer bulk given by $E_i=V_{bi}/d$, where V_{bi} is the built-in potential and d the thickness of the polymer layer. Recent studies of the $I-V$ curves of various diodes under illumination have shown that $V_{\text{bi}} = \Delta W/e$, where ΔW is the difference between the metal and ITO electrode work functions.[13] This was demonstrated by measuring the photovoltage at saturation $V_0 = V_{\text{bi}}$ which is the value at which the $I-V$ curve under illumination crosses the dark curve. In particular, in an Al/MEH–PPV/ITO LED ΔW was measured to be 0.7 eV.[14] In order to check the validity of the E_F pinning model, the $I-V$ curves of the PDEPDPV devices were, therefore, measured under various illumination conditions. As shown in Fig. 3(b) illumination of such a device at 100 mW/cm^2 (saturation) also yields a symmetric $I-V$ curve, although the photocurrent is ~2 orders of magnitude larger than the dark current. Yet $V_0 \approx 0$ in Al/PDEPDPV/ITO, in contrast to the value of $V_0 \approx 0.7$ V in Al/MEH–PPV/ITO mentioned above.[13,14] The nearly zero saturated photovoltage in the present devices shows that indeed $E_i \approx 0$ within most of the polymer layer and is not determined by ΔW, which remains 0.7 eV. The lack of a substantial photovoltaic effect in the PDEPDPV structures is a direct manifestation of Fermi energy pinning in these devices.

A constant semiconductor-metal barrier height, independent of the metal work function, was previously reported for CdSe and various metals.[15] This phenomenon was assigned to the covalent nature of the material which is responsible for the location of the surface state in the middle of the gap. This is in contrast to ionic materials in which the surface states are located near the band edges.[16]

For polymer LEDs, basic tunneling theory predicts[12]

$$I \propto V^2 \exp(-b/V), \tag{1}$$

where $b = 4(2m^*)^{1/2}\phi^{3/2}d/(3eh)$ for a triangular barrier of height ϕ and m^* is the effective mass of the carrier. A plot of $\ln(I/V^2)$ versus I/V, based on Fig. 1, is shown in Fig. 4(a).[3] It indicates that Eq. (1) fits the observed behavior from 14 to 21 V, but substantially deviates from it at low bias voltages. Nevertheless, substituting the free-electron mass for m^* yields $\phi = 0.2$ and 0.19 eV for forward and reverse bias, respectively. These values are not inconsistent with other reports which fit $I(V)$ curves of polymer LEDs to Eq. (1).[12]

One-step tunneling is not expected to be valid at low voltages, since the tunneling distance $x = d\phi/V$ is then too large. For example, $x > 100$ Å at $V = 1$ V and $d = 1000$ Å. It has, therefore, been suggested that the excess injection current at low V is due to sequential tunneling of carriers via localized states near E_F.[17] That model predicts the relationship

$$\ln(I) = -\gamma\left(\frac{d}{V}\right)^{1/2}, \tag{2}$$

where $\gamma = 4(\Gamma/3)^{1/2}(2m^*/e^2h^2)^{1/4}\phi^{3/4}$, $\Gamma = -\ln(p)$, and p is the probability that a carrier will find another localized state with an energy close to E_F. Figure 4(b) displays $\ln(I)$ versus $V^{-1/2}$ for the PDEPDPV diode. The curve is linear for $V < 13$ V, which is just below the bias range at which Eq. (1) fits the results. Moreover, Eq. (2) yields $p \approx 1$ for $\phi = 0.2$ eV. From the large value of p we postulate a large density of localized states at E_F (consistent with Fermi level pinning by surface states), which provides an alternative mechanism for carrier injection at low V.

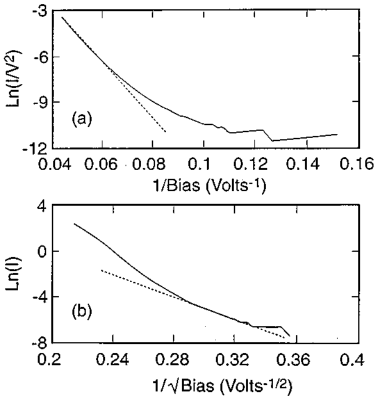

FIG. 4. $I-V$ plots of a typical PDEPDPV device measured at $T = 77$ K: (a) $\ln(I/V^2)$ vs $1/V$; (b) $\ln(I)$ vs $V^{-1/2}$.

In summary, novel light-emitting Al/PDEPDPV/ITO devices display unusual symmetric $I-V$ and electroluminescence-voltage behavior. These are found to be consistent with a high density of deep gap states at the electrode/polymer interfaces which pin the Fermi level E_F. The carrier injection mechanisms have been identified. At high bias voltage it is due to one-step carrier tunneling; at low bias voltage, however, multiple tunneling steps among localized states near E_F is dominant.

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