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Quinquethiophene light-emitting diodes with molecular dimensions

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Light-emitting diodes using Langmuir-Blodgett films of quinquethiophene as the emitting layer have been fabricated, and electrically and optically characterized. By utilizing additional layers of electron-transporting materials, the emitting material thickness has been reduced down to a single monolayer without serious decrease in the quantum efficiency. These electronic devices are valuable tools for studying carrier injection and transport, exciton formation, and quenching on a real molecular scale. [S0163-1829(96)03547-3]

INTRODUCTION

The invention of advanced methods such as molecular-beam epitaxy and electron-beam lithography have made the fabrication of mesoscopic inorganic devices possible. However, a different approach to even smaller devices is to use organic molecules as active elements instead of structures defined in bulk materials.[1] Organic transistors,[2] photochemical switching devices,[3] rectifiers,[4] bacteriorhodopsin electro-optical devices,[5] and tunneling structures[6] have been reported, and can be considered as early demonstrations of molecular electronics. In the cases listed above the Langmuir-Blodgett (LB) technique has been used to fabricate the active layers.

The report on the first light-emitting diode (LED) based on conjugated polymers[7] launched a worldwide research on polymer LEDs. Since then, a variety of polymer and oligomer LEDs have been reported.[8] In most cases, thick spin-cast or vacuum-evaporated films have been used, but also organic LEDs based on thick multilayer LB films have been reported.[9–11] However, the full potential of the LB technique for device fabrication was not used in any of this work.

The advantage of the LB technique is that carefully defined layered (hetero)structures with small thickness dimensions can be fabricated. We recently reported on quinquethiophene (QT) LEDs where the emitting film consisted of only five highly ordered LB layers.[12,13] In this paper we show that the thickness of the emitting region can be further reduced to a single QT LB monolayer in a heterostructure device where a few additional LB layers of 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) are used as electron-transporting films, and indium-tin-oxide (ITO) and aluminum are used as anode and cathode electrodes, respectively.

EXPERIMENT

LEDs were fabricated on glass substrates partly covered with ITO having a sheet resistance less than 10 Ω/□ (kindly supplied by Planar International Ltd). Emitting layers of QT mixed with arachidic acid (60/40 mol. %) and electron-transporting layers of PBD mixed with arachidic acid (10/90 mol. %) were deposited by using the LB technique at surface pressures of 30 and 20 mN/m, respectively, with a subphase of 0.5-mM $CdCl_2$. QT was synthesized as described elsewhere.[14,15] Thermal stress during the evaporation of the aluminum upper electrode was minimized by using a small-size evaporation source and by maintaining the substrate at room temperature. The LED area was typically ≈ 0.1 cm^2. A variety of devices with different numbers of layers were deposited on each substrate, all of them giving consistent results.

The electroluminescence (EL) intensity was measured using a calibrated silicon photodiode and a Keithley 617 electrometer, and the current-voltage ($I-V$) curves using a Keithley 230 voltage source and a Keithley 2001 digital multimeter. The sample was stored in vacuum and measured in nitrogen atmosphere, but moved and handled in air.

RESULTS AND DISCUSSION

The use of electron-transporting layers of PBD in LEDs has several advantages. At the QT-PBD heterojunction a barrier is formed which partly blocks the hole current, and results in a situation where the electron injection from aluminum more closely matches the hole injection from ITO. Thus the quantum efficiency (η) increases[8,13] (η is defined as the ratio of the number of photons emitted to the number of charges passing through the device). Furthermore, the PBD layers protect the emitting QT layers from short circuits due to the penetration of aluminum, as well as from chemical reactions[16] with the metal. To fabricate LEDs with less than about five QT layers, additional PBD LB layers are essential, allowing us to reduce the thickness of the emitting material down to monomolecular scale.

We first optimized the thickness of the PBD film. The LEDs used for optimization studies consisted of a QT film, typically 13 layers thick, covered with zero, four, or ten PBD layers. Although the current was found to decrease with an increasing number of PBD layers, the EL intensity vs current characteristics and η were practically identical for devices with 4–10 PBD layers, while devices with no PBD gave a lower luminance and η, in agreement with Ref. 13. Figure 1 shows η as a function of PBD film thickness. Based on these results, we used six or eight PBD layers in later experiments.

The $I-V$ characteristics of several samples were measured, and found reproducible. Typical $I-V$ curves of heterostructure LEDs with one, three, or seven QT and six PBD layers are presented in Fig. 2. These curves obtained for the first scan indicate a current maximum at about 2–2.5 V, and

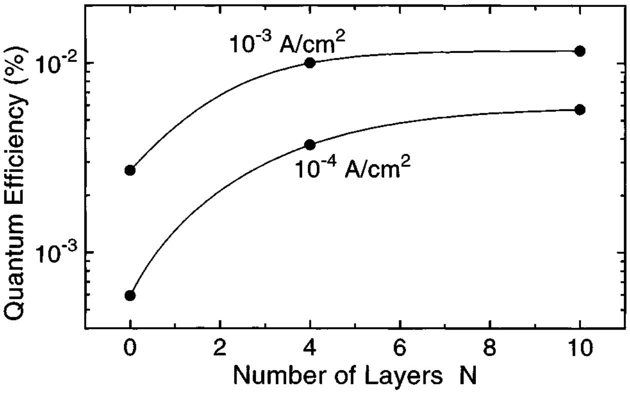

FIG. 1. Quantum efficiency vs number of PBD layers for a structure ITO-QT (13 layers)-PBD (N layers)-aluminum at 1×10^{-4} and 1×10^{-3} A/cm^2. The lines are only to guide the eye.

an increase in current above 4 V. The former feature, which was especially clear for the thinnest QT films, appeared only for the first scan, and did not induce a corresponding increase in the EL intensity. A similar ''current anomaly'' has recently also been observed for spin-cast poly(p-phenylene vinylene) LEDs, where it is due to the changes in the doping concentration during operation.[17] In our case, the anomaly is strongest in QT/PBD structures with thinnest QT films. The thin QT-PBD heterostructure LEDs did not rectify, and the $I-V$ curves for positive and negative biases are relatively symmetrical. Earlier, symmetrical behavior was also reported for polymer LEDs.[11,18] The absence of real rectification could be due to the small device thickness,[11] a built-in field, a reaction or an oxide barrier at the aluminum interface,[18] and/or dopant diffusion.[19] Also interesting is the fact that the current does not increase but, further, decreases slightly with the decreasing number of QT layers from seven to one, even though the average electric field increases at the same time. Similar behavior has been observed in thin poly(3-hexylthiophene) LB LEDs.[20] This could be due to a higher band gap, and, correspondingly, to a higher barrier in the thinnest QT films compared with thicker ones.[21] Thus, for a constant field, the current should be smaller for thinner QT films, in agreement with experiments.

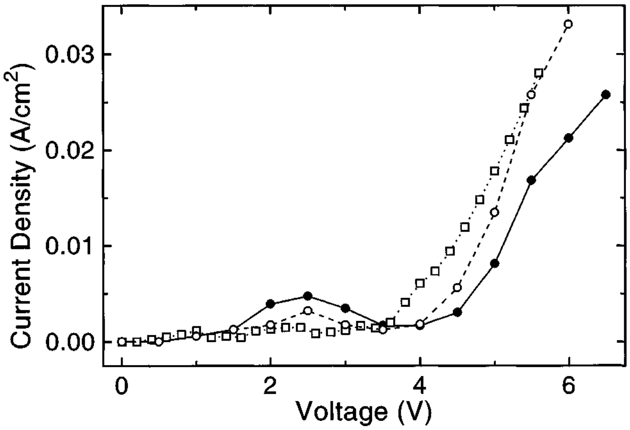

FIG. 2. Current-voltage characteristics of ITO-QT-PBD-aluminum devices with one (solid circles), three (open circles), and seven layers (squares) of QT, and six layers of PBD. The results are for the first scan and forward bias [ITO(+), aluminum(−)]. The lines are only to guide the eye.

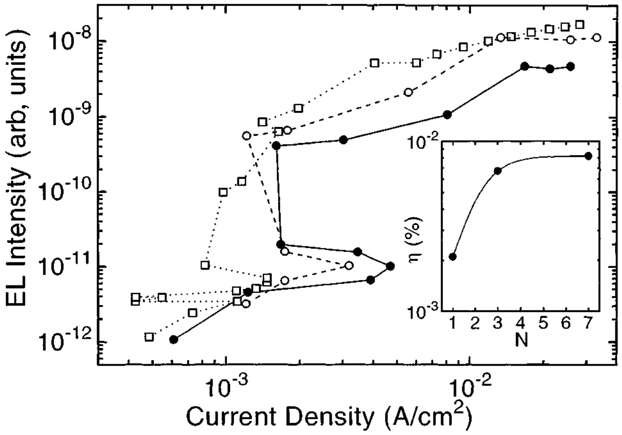

FIG. 3. The EL intensity vs current characteristics of the device (see the caption of Fig. 2). The inset gives the quantum efficiency vs number of QT layers at 1×10^{-2} A/cm^2 (solid circles).

The photoluminescence (PL) and absorption spectra of QT LB films are redshifted and blueshifted, respectively, compared with solutions, indicating H aggregates in the LB film.[15] The EL was easily detectable by using a silicon photodiode, although the exact EL spectrum of the thinnest devices could not be measured because of the short lifetime, ≈1 min, under operation. However, the EL spectra of LEDs with QT LB multilayers but no PBD could be measured, and were found to be similar to the PL spectrum.[12,13] The EL band was found to be located in the 2.1–2.5 eV region.

The EL intensity vs current curves for the first scan are shown in Fig. 3. Contrary to the $I-V$ curves, these characteristics were highly unsymmetrical: only forward-biased LEDs gave EL. The S form of the curve is due to the ''current anomaly,'' especially strong for the thinnest QT films. At a fixed current the EL intensity slightly increases with an increasing number of QT layers, but saturates at about three layers. As shown in the inset of Fig. 3, η was about 7–8$\times10^{-3}$% for seven or more QT layers, 6$\times10^{-3}$% for three QT layers, and 2$\times10^{-3}$% for a single QT layer at 1×10^{-2} A/cm^2. Reference structures with only PBD did not operate as LEDs, and their EL intensity and η were orders of magnitude lower than those of heterostructure devices.

Hole injection from ITO to QT is relatively easy, and holes accumulate at the heterointerface. Because of the excess of holes, some reach the cathode without forming excitons. On the other hand, in the case of a thick QT film, it is reasonable to assume that all electrons injected form excitons, and thus that the EL intensity is proportional to the electron injection rate while the current through the device is equal to the hole injection rate.[12,13] For the thinnest QT films η decreases, as shown in the inset of Fig. 3. We relate the decrease in η to nonradiative processes at the ITO-QT interface. Because of the thinness of the QT film, some electrons may reach the ITO electrode and become lost without forming excitons. Similarly, excitons formed near the QT-PBD interface may reach the ITO-QT interface and become quenched due to surface recombinations or due to electron/energy transfer to ITO (see, e.g., Refs. 22 and 23 and references therein). On the other hand, the band gap of PBD is higher than that of QT, preventing excitons from moving from QT to PBD. The fact that η decreases with decreasing QT film thickness, and saturates to a constant value for thicknesses above three layers, indicates that it is reasonable to assume that the excitons are formed within less than three QT monolayers nearest to the PBD interface, and the nonradiative processes due to the ITO-QT interface have a very short ''range,'' less than three layers.

Electrons are lost or excitons quenched by the metallic ITO electrode if they reach it by drift or diffusion.[23] The electron transit time is $t_r = d_{\mathrm{QT}}/(\mu_n F)$ and the diffusion length $L_n = \sqrt{D_n \tau_n}$, where d_{QT} is the QT film thickness, μ_n the electron mobility, F the electric field, D_n the diffusion constant, and τ_n the lifetime. The exciton diffusion length is $L_{\mathrm{exc}} = \sqrt{D_{\mathrm{exc}} \tau_{\mathrm{exc}}}$, where D_{exc} is the exciton diffusion constant and τ_{exc} the lifetime. Efficient EL is obtained only if $t_r \geqslant \tau_n$ and $d_{\mathrm{QT}} \geqslant L_n, L_{\mathrm{exc}}$.[24] Based on the experiments, we assume that one of the conditions $t_t \approx \tau_n$, $d_{\mathrm{QT}} \approx L_n$ or $d_{\mathrm{QT}} \approx L_{\mathrm{exc}}$ is reached for d_{QT} of the order of a QT LB monolayer, ≈ 2.5 nm. For example, assuming reasonable values $\mu_n \approx 10^{-8}$ cm^2/V s and $F \approx 10^6$ V/cm, and calculating D_n via the Einstein relation, an upper limit of about 30 μs is obtained for τ_n, defined by the drift process (the diffusion process giving a higher upper limit of ≈ 200 μs for τ_n). Furthermore, for a typical lifetime $\tau_{\mathrm{exc}} \approx 1$ ns,[25] the exciton diffusion constant D_{exc} is, at most, $\approx 10^{-4}$ cm^2/s in QT LB films. Short diffusion lengths of a few nm are quite realistic for organic materials.[26]

CONCLUSIONS

We have fabricated interesting heterostructure LEDs using LB films of QT and PBD as the active emitting and electron-transporting layers, respectively. The LB technique allowed us to decrease the thickness of the emitting region to a single monolayer of about 2.5 nm. The quantum efficiency, approaching 10^{-2}%, is surprisingly insensitive to the thickness of the QT film, indicating that exciton formation and recombination take place in less than about three QT monolayers at the QT-PBD interface. Correspondingly, the nonradiative processes at the ITO-QT interface have a very short range due to the difficult transport of electrons and excitons. To increase the quantum efficiency further, one should more carefully balance the injection of holes and electrons by using other electrode materials, and decrease the rate of nonradiative recombinations in QT. Other thiophene derivatives or more suitable device structures could also be beneficial.

In our work we did not try to minimize the lateral dimensions of the device. However, as the active region is based on an *ordered molecular film*, it should be possible to reduce the area significantly without seriously affecting the operation. In principle, individually contacted QT aggregates or QT molecules (area ≈ 0.2 nm^2) within the insulating fatty acid matrix could form LEDs in analogy with recent studies in polymer blend LEDs.[27] Further work along these lines is needed.

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