Organic quantum well light emitting diodes

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ABSTRACT

This work reports on simulation and experimental investigation into the charge transport and electroluminescence in a quantum well (QW) organic light emitting diode (OLED) consisting of a N,N′-di(naphthalene-1-yl)-N,N′-diphenylbenzidine (NPB) as a hole transport layer, tris (8-hydroxyquinoline) aluminum (Alq3) as a potential barrier and electron transporting layer, and rubrene as potential well layer. Indium tin oxide was used as an anode, while LiF/Al was employed as a cathode. The carrier transport was simulated using one-dimensional time-independent drift-diffusion model. The influence of the well width, barrier width, and the number of QWs on the carrier distribution, recombination rate, and device performance was investigated. Finally, the device structures which yielded most promising simulation results were fabricated and characterized. The comparison between the experimental and theoretical results is discussed.

Keywords: OLEDs

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted considerable attention in the field of flat panel displays due to their potential to offer thinner, brighter displays with a wider viewing angle [1-3]. It is well documented that optimum efficiency can be achieved when electron and hole density are well-balanced in the emission region [4]. However, in conventional N,N′-di(naphthalene-1-yl)-N,N′-diphenylbenzidine (NPB)/ tris (8-hydroxyquinoline) (Alq3) bi-layer devices, the mobility of holes in NPB is much larger than the mobility of electrons in Alq3. This leads to unbalanced carrier concentration, which results in the lowering of recombination efficiency. Solutions such as employing different device structures or using different hole transporting material have been proposed in order to lower the hole mobility, thus improving the balance of carrier density [5-7].

Recently, organic multiple-quantum-well (MQW) structures have been reported to successfully reduce hole mobility, enable achievement of narrower emission and enhance emission intensity [8, 9]. On the other hand, rubrene has been widely used as a dopant in the host material, to improve the emission efficiency of OLED devices due to its unique hole trapping characteristic [10]. Holes and electrons directly recombine on a rubrene molecule with very high fluorescence efficiency [11-13], which makes it a suitable emissive material. We demonstrate here that by combining both unique properties of quantum wells (QWs) and the rubrene material, a device with balanced carrier transport and high luminance can be realized.

In this work, we simulate electrical carrier transport characteristics of a MQW OLED device and investigate the influence of well width and the number of QWs on the carrier distribution, electric field and recombination rate. NPB was used as hole transport layer and Alq3 was used as a potential barrier and electron transporting layer, and rubrene as potential well layer. These organic layers are sandwiched between a LiF/Al cathode and ITO anode to provide efficient carrier injection. Glass with 1 mm thickness was used as substrate. The optimum device was fabricated and characterized. The calculated optical emission spectrum is then compared with the experimental result. The paper first describes the optical and electrical simulation models used including the simulation parameters and simulated experimental conditions. The outcome of simulation and experimental result is then discussed.
2. DESCRIPTION OF THE MODEL

2.1. Electrical model
In the organic semiconductor the electrical transport is modeled by the one-dimensional time-independent drift-diffusion model [4, 14, 15], which solves for a self-consistent solution of electron density, \( n \), hole density, \( p \) and potential \( \psi \) using the semiconductor solver Atlas [16]. The model consists of the continuity equation and the Poisson equation. The continuity equation for \( n \) (electrons) and \( p \) (holes) is given by

\[
\frac{d}{dx}(-\mu_n \frac{dn}{dx} + D_n \frac{dn}{dx}) = R
\]

\[
\frac{d}{dx}(\mu_p \frac{dp}{dx} + D_p \frac{dp}{dx}) = R
\]

where \( \mu_n \) and \( \mu_p \) are the electron and hole mobilities, \( D_n \) and \( D_p \) are diffusion constants and \( R \) is the recombination rate. The \( \mu \) and \( D \) are related by the well known Einstein relation. The carrier mobilities are modeled by the field-dependent form:

\[
\mu_n(E) = \mu_{n0} \exp \left( \frac{E}{E_0} \right)
\]

\[
\mu_p(E) = \mu_{p0} \exp \left( \frac{E}{E_0} \right)
\]

where \( \mu_{n0} \) and \( \mu_{p0} \) are the zero field mobilities, \( E \) is the electric field and \( E_0 \) is the constant known as characteristic field. The recombination rate is taken to be optical only and modeled by the Langevin recombination coefficient \( \gamma \) [15, 17]:

\[
R_{opt} = \gamma (pn - n_i^2)
\]

\[
\gamma = \frac{4\pi e \mu_R}{\varepsilon_r \varepsilon_0}
\]

where \( n_i \) is the intrinsic concentration and \( \mu_R \) is effective recombination mobility, taken to be the larger of the electron and hole mobilities in the material, \( \varepsilon_r \varepsilon_0 \) is the permittivity of the material. The effect of traps in the organic layers is not included in the current electrical model as the literature indicates the inclusion of traps has no significant effect on the simulation results obtained [15]. Poisson’s equation is used in the form

\[
\frac{d^2 \psi}{dx^2} = -\frac{e}{\varepsilon_r \varepsilon_0} \left[p(x) - n(x) + N_D - N_A\right],
\]

where \( N_D \) and \( N_A \) are the ionized donor and acceptor dopant concentrations.

These equations are solved for the p-n junction structure using Schottky contact boundary conditions between a metal (which also serves as the reflecting surface for optical modeling) and the organic layer at the anode and the cathode. The barrier heights governing carrier injections are: \( \phi_{bn} \) for electrons and \( \phi_{bp} \) for holes and are related to the metal work function \( \phi_m \) of the electrodes and the electron affinity of the organic material \( \chi_c \):

\[
\phi_{en} = (\phi_m - \chi_c)
\]

\[
\phi_{hp} = (E_g - \phi_{bn}) = E_g - (\phi_m - \chi_c)
\]

The continuity equations and the Poisson equation are solved to obtain the carrier concentrations, electric field distributions and recombination rate. The thickness of recombination region can be determined from the recombination rate, which can be used to estimate the width of emission region (taking into account of exciton diffusion) to be included into the optical model.
2.2. Parameters used in electrical simulation

The material parameters used for modelling of carrier transport are obtained from literature [4, 13-15, 18, 19]. The devices were simulated with forward bias of 5 V. The mobility of majority carriers in the organic materials has been set to be two orders of magnitude higher than its minority carriers. Where the simulation model requires a large number of material parameters only a few critical parameters including barrier heights to carrier injection, bandgaps of the organic materials and carrier concentrations have marked effects on the simulated result [14].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NPB</th>
<th>Alq3</th>
<th>Rubrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Permittivity</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>$\mu_{no}$ (cm$^2$/Vs)</td>
<td>$6.1 \times 10^{-6}$</td>
<td>$1.9 \times 10^{-6}$</td>
<td>$9.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\mu_{po}$ (cm$^2$/Vs)</td>
<td>$6.1 \times 10^{-4}$</td>
<td>$1.9 \times 10^{-8}$</td>
<td>$9.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>$E_0$ (V/cm)</td>
<td>$4.44 \times 10^5$</td>
<td>$7.1 \times 10^4$</td>
<td>-</td>
</tr>
<tr>
<td>$N_c$ (cm$^{-3}$)</td>
<td>$1.1 \times 10^{21}$</td>
<td>$1.1 \times 10^{21}$</td>
<td>$1.1 \times 10^{21}$</td>
</tr>
<tr>
<td>$N_v$ (cm$^{-3}$)</td>
<td>$1.1 \times 10^{21}$</td>
<td>$1.1 \times 10^{21}$</td>
<td>$1.1 \times 10^{21}$</td>
</tr>
<tr>
<td>$N_d$ (cm$^{-3}$)</td>
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<tr>
<td>$E_g$ [eV]</td>
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<td>2.7</td>
<td>2.2 [13]</td>
</tr>
<tr>
<td>$\chi_c$ [eV]</td>
<td>2.4</td>
<td>3.0</td>
<td>3.2 [13]</td>
</tr>
</tbody>
</table>

Table 1 Electrical simulation parameters

2.3. Optical model

The intensity of the light output in the form of the electroluminescence (EL) spectrum was calculated using a method [20-25] based on the equivalence between the probability of photon emission and the power radiated by a classical dipole antenna.

Consider the structure shown in Fig. 1. It can be seen as consisting of multiple thin film layers stacked on top of each other. In a layer with complex refractive index $N_i$, the amplitude of the wave vector is given by:
where $\lambda$ is the emission wavelength in vacuum. The complex refractive index for each layer of the device was measured using Variable Angle Spectroscopic Ellipsometry (VASE) and fitted using the Lorentz-Drude model [26-28].

When considering wave propagation through thin film layers, it is convenient to resolve the wave vector into two components: the component normal to the direction of propagation and the component along the direction of propagation (we use the z-axis as the axis of propagation), which is given by:

$$\kappa = k_i \sin(\alpha_i),$$

and

$$k_{z,i} = k_i \cos(\alpha_i) = \sqrt{k_i^2 - \kappa^2},$$

respectively, where $\alpha_i$ is the angle the wave makes with the z-axis.

The total power $F$ emitted by a dipole antenna located within the multilayer structure normalized to the power output of the same dipole in an infinite medium is given by:

$$F = \int_0^\infty K(\kappa) d\kappa^2,$$

where $K$ is the power density per unit $d\kappa^2$.

The power density ($K$) can be resolved into the TM and TE component, with each component separated into power densities for dipoles oriented parallel and perpendicular to the z-axis. With this in mind, the power densities can be defined as:

$$K_{\perp}^{TM} = \frac{3}{4} \Re \left[ \frac{k_e^2 k_{z,e} \left( 1 - a_{-}^{TM} \right) \left( 1 - a_+^{TM} \right)}{k_e^2 k_{z,e} \left( 1 - a_{-}^{TM} \right) \left( 1 - a_+^{TM} \right)} \right],$$

$$K_{\perp}^{TE} = 0,$$

$$K_{\parallel}^{TM} = \frac{3}{8} \Re \left[ \frac{k_{z,e} \left( 1 + a_+^{TM} \right) \left( 1 + a_{-}^{TM} \right)}{k_e^2 \left( 1 - a_{-}^{TM} \right) \left( 1 - a_+^{TM} \right)} \right],$$

$$K_{\parallel}^{TE} = \frac{3}{8} \Re \left[ \frac{1}{k_e k_{z,e} \left( 1 - a_{-}^{TE} \right) \left( 1 - a_+^{TE} \right)} \right],$$

where $e$ denotes the emissive layer (sandwiched between top and bottom mirrors) and $a$ is the reflection coefficient of the mirror with respect to the location of the dipole, defined as:
\[ a_{\pm/}^{TM/TE} = r_{e,+/-}^{TM/TE} \exp(-2jk_z a_{\pm/} e^{z_{\pm/-}}), \]  

(14)

\[ a_{-/}^{TM/TE} = a_{+/-}^{TM/TE} a_{-/}^{TM/TE}, \]  

(15)

where \( z_+ \) is the dipoles' distance from the top mirror, \( z_- \) is the dipoles' distance from the bottom mirror and \( r \) is the amplitude reflection coefficient of the top and bottom mirrors calculated using the modified transfer matrix approach of Katsidis and Siapkas to account for partially coherent superposition of waves in the thick substrate [29, 30].

For randomly oriented dipole antenna (equal probability for all orientation directions), the power density is given by:

\[ K_{TM,TE} = \frac{1}{3} K_{\perp,TE}^{TM,TE} + \frac{2}{3} K_{\parallel,TE}^{TM,TE}. \]  

(16)

The overall power density will then be the average of the TM and TE component.

3. EXPERIMENTAL DETAILS

The materials used (Alq3 and NPB from H. W. Sands Corp., and rubrene from Aldrich) were purified by vacuum sublimation before fabrication. ITO substrates with nominal sheet resistance of 40 \( \Omega \)/square were supplied by Varitronix Limited, Hong Kong. All the ITO substrates were cleaned before fabrication with the following cleaning procedure: the substrates were first rinsed by ethanol, acetone, toluene, then acetone, ethanol, and deionized (DI) water. After that, the substrates were cleaned in ultrasonic bath for 10 minutes in acetone, ethanol, and DI water, and dried in an oven at around 90 degree Celsius. 15 minutes UV-ozone treatment was performed immediately before placing ITO inside the evaporator.

Devices were fabricated by vacuum deposition. The pressure during evaporation was of the order 10^{-4} Pa. The evaporation rate was kept at \(-1 \) \( \AA/\)s. The distance from source to film was about 23 cm to ensure uniformity of film thickness, and the substrate holder was rotating. The thickness of the films was controlled by a quartz thickness monitor. The electrode consisted of 0.5 nm LiF and 100 nm Al. Six cells were fabricated on each ITO substrate in one fabrication. The electroluminescence (EL) spectra were measured using Control Development fiber optic spectrometer (PDA 512 USB), while luminance-current-voltage (L-I-V) characteristics were measured in ambient environment using a Keithley 2400 sourcemeter and luminance meter (Minolta LS-100).

4. RESULTS AND DISCUSSION

Electrical and optical models outlined in the previous sections were used to investigate the characteristics of organic QW structures consisting of alternate layers of Alq3/Rubrene or NPB/Rubrene shown in Fig. 2. The electrical properties including carrier concentration, electric field and recombination rate have been investigated and the results of the electrical model were used in optical modeling to obtain simulated electroluminescence. The structure of the QW based OLED under investigation was:

\[
\text{ITO/NPB(60 nm)/}\{\text{Alq}_3(5 \text{ nm)/Rubrene(1 nm)}\}_{n/}\text{Alq}_3/\text{LiF/Al,}
\]

\[
\text{ITO/NPB(60 nm)/}\{\text{NPB(5 nm)/Rubrene(1 nm)}\}_{n/}\text{Alq}_3/\text{LiF/Al,}
\]

Where \( n \) designates the number of QWs used in the device. High work function ITO was used as hole injection anode and LiF/Al as cathode due to its barrier lowering effect which would facilitate improved electron injection. NPB with thickness of 60 nm was used as a hole transporting layer. Alternate layer of Alq3(5 nm)/Rubrene(1 nm) was used to confine the carriers and locate the recombination region within the QW. The Alq3 layer was used as electron transporting layer. The total organic layer thickness was kept at 120 nm, while the thickness of the Alq3 layer next to cathode was adjusted accordingly.
The electric field and carrier density of Alq3 based single well device was simulated and the results are shown in Fig. 3. When a forward bias voltage of 5 V was applied, holes were injected from anode into the NPB/Alq3 layer and accumulated in the rubrene layer due to bandgap offset. The Alq3 layer adjacent to the cathode acts as an electron transporting layer and a hole blocker in this case, where accumulation of holes in the rubrene/Alq3 region caused electric field in Alq3 region to be higher than that of NPB layer according to Poisson’s equation. The simulation shows, at steady state, the majority of holes is trapped in the rubrene layer and recombines with the electrons coming from ETL.

Figure 3: Simulated electric field and carrier density of Alq3 based single QW device.

Figure 4 compares the simulated carrier recombination rate in the control bi-layer device and a single Alq3/rubrene QW device. In the control bi-layer device, recombination region is positioned in the Alq3 layer, within 5nm from the NPB/Alq3 interface. On the other hand, in the single QW device, majority of recombination process happens within rubrene, which acts as a QW between the two adjacent Alq3 layers. In this device, holes are accumulated and confined in the rubrene layer due to the existence of the barrier. When electrons injected from cathode arrive this region, direct recombination process occurs which leads to the high recombination rate. It can be observed that the recombination rate in QW device is a several orders of magnitude higher than in the control device and clearly confined within the QW region. When another pair of Alq3/rubrene layers is inserted (see Fig. 5), recombination occurs in both rubrene QW...
layers, with higher recombination rate in the first well. With the introduction of the third QW to the device, we observe
the same behavior; the recombination is once again confined to the rubrene QW regions. However, the magnitude of
recombination within the third well is a several orders of magnitude below that in the 1st and 2nd QW. The highest
recombination in the first QW may be attributed to the fact that when holes are transported through the organic layers,
rubrene acts as a hole trapping layer and recombination center. Therefore, the recombination is always highest in the 1st
and 2nd well and gradually decreases as the number of wells is increased.

For the NPB/rubrene QW devices, the recombination enhancement and confinement of the recombination process to the
QW region are not as prominent as in Alq3/rubrene based QW devices. This is likely due to the higher hole mobilities in
NPB than Alq3, and its reduced ability to slow down the hole transportation towards rubrene layer, thus leading to
unbalanced carrier concentration. We also investigated the effect of well thickness on the recombination rate. By
increasing the well thickness from 1 nm to 2 nm, the recombination region is still confined in the rubrene material.
However, no prominent difference has been observed on the distribution of recombination region within the well, in
most cases the recombination is evenly distributed across rubrene layer and not accumulating toward adjacent interfaces.

Figure 4: Simulated carrier recombination rate of ordinary bi-layer device and Alq3 based single QW device.

Figure 5: Simulated carrier recombination rate of Alq3 based double and triple QW device.

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The NPB/Alq$_3$ bi-layer control device and the Alq$_3$/rubrene based single and double QW devices were fabricated and characterized. The comparison between the simulated and experimental electroluminescence (EL) spectrum (for normal viewing angle) is shown above. The luminance spectrum for the bi-layer device was simulated with the emission layer thickness of 10 nm based on the recombination region thickness obtained from the electrical model. The simulation results match the main features of experimental spectrum very well. For both the single and the double QW devices, the simulated result show a shoulder around 650 nm which is not observed in the experiments, but the model properly predicts some green emission from Alq$_3$ at 520 nm and the peak of the simulated emission spectrum corresponds well to the rubrene emission obtained from experiment.

5. CONCLUSION

We have simulated both electrical and optical behaviors of the MWQ OLEDs using numerical and analytical models. By employing MQW structure together with rubrene as a QW material, we were able to trap and confine holes within the QW region creating enhancement in the recombination rate. Optimum recombination rate is achieved in the Alq$_3$ based single or double quantum-well device, due to low hole mobility in the Alq$_3$ layer thus leading to more balanced carrier density in the rubrene emissive layer. Increasing the well width has negligible effect on the distribution of recombination within the well as no accumulation towards adjacent well is observed. Good agreement between the simulated and experimental electroluminescence spectra was observed in the Alq$_3$ based QW OLED devices.

REFERENCES


