Charge carrier mobility of mixed-layer organic light-emitting diodes

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(Received 26 February 2007; accepted 30 August 2007; published online 3 October 2007)

The authors report the investigation of the charge transport behaviors in mixed thin films of N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine and tris(8-hydroxyquinoline) aluminum. The extracted electron and hole drift mobility were found to be sensitive to the compositional fraction and interpreted by energy levels, charge mobilities of neat compounds, and microscopic networks within the mixed systems. The carrier conduction characteristics, therefore, were used to illustrate the electrical and optical properties of the organic light emitting devices with a mixed layer and present direct evidences on the role of the mixed layer in these devices.


A mixed organic layer in the device structure has attracted wide attention for organic light-emitting diodes (OLEDs), organic solar cells and organic field effect transistors, because it potentially provides another degree of freedom to improve the device performance. Aziz et al. demonstrated that it is possible to resolve the device reliability problem by using a mixed HTL-ETL layer as the emitting layer (EML). The intention was to blur the energy barrier of the HTL/ETL interface and to improve the carrier balance, thus reducing the production of cationic tris(8-hydroxyquinoline) aluminum (Alq3) species. In previous efforts, we showed that the bipolar transport characteristic of the mixed EML helps to reduce driving voltage and to elongate device lifetime. These performance evidences of the mixed-layer OLEDs render the investigation of the charge mobility of the mixed layer a critical step for taking advantage of this extra degree of freedom in optimizing OLEDs and other organic electronic devices. In this report, we present a time-of-flight (TOF) study of the drift mobility of hole and electron in mixed thin films of N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB) and Alq3. The luminescence–current–voltage (L–I–V) and electroluminescent (EL) spectra of the OLEDs which are composed of a thin film with different compositional fractions of the two materials are reported as well. The correlation between the extracted charge mobility of the mixed layer and the performance of the corresponding mixed-layer OLED is illustrated.

The TOF samples have a glass/ITO (100 nm)/organic layer (100 nm)/Al(20 nm) configuration. In addition to neat NPB and Alq3 samples, the mixed thin films with different NPB compositional fractions (CN=75%, 50%, and 25%) were prepared by coevaporation, where CN is the compositional fraction of NPB. In the TOF measurement, 5 ns Nd:YAG laser pulses at 355 nm were incident to the ITO or semitransparent Al side to create photoexcited carriers. The excitation power density was set at ~1.6 W/cm² to avoid space-charge effect. The instrumental response time was kept much shorter than the transit time. The transient photocurrent was recorded by measuring the voltage across a 50 Ω resistor with a 1 GHz digital oscilloscope. The device structure of the EL samples is ITO/NPB (20 nm)/EML (80 nm)/Alq3 (20 nm)/LiF (1 nm)/Al (100 nm). Both the TOF and EL samples were completed with encapsulation in a glovebox. The active area is 16 mm². All measurements on these encapsulated samples were carried out at room temperature.

Figure 1 shows the field dependence of hole and electron drift mobility of neat films of NPB and Alq3, as well as the NPB-Alq3 composite films. The measured mobilities of neat films of NPB and Alq3 agree with the ones obtained previously. In particular, the electron mobility of the neat Alq3 film at 80 V/μm is very close to the one determined by photoinduced electroluminescence in which the film thicknesses are 150–200 nm, indicating that the impurity problem for the thick samples (>1 μm) film is insignificant. Since the introduced traps are uniformly distributed within the or-
The hole and electron mobilities ($\mu_h$ and $\mu_e$, respectively) vs the square root of the applied electric field ($E^{1/2}$) of NPB-Alq3 composite films prepared with five NPB volume fractions ($C_N$). □, $C_N=100\%$; ○, $C_N=75\%$; △, $C_N=50\%$; ▽, $C_N=25\%$; ●, $C_N=0\%$.

FIG. 1. (a) Hole and (b) electron mobilities ($\mu_h$ and $\mu_e$, respectively) vs the square root of the applied electric field ($E^{1/2}$) of NPB-Alq3 composite films prepared with five NPB volume fractions ($C_N$). □, $C_N=100\%$; ○, $C_N=75\%$; △, $C_N=50\%$; ▽, $C_N=25\%$; ●, $C_N=0\%$.

organic layers which were prepared in our evaporation system, the influence of the introduced traps to the mobility is expected to be similar for different thicknesses. The field-dependent charge mobility was analyzed with the Poole-Frenkel model for Coulombic trap controlled transport: $\mu = \mu_0 \exp(\beta E^{1/2})$, where $\mu_0$ is the field-free mobility and $\beta$ is the Poole-Frenkel constant. The detailed analysis of these TOF results will be given in a later publication. Here, we focus on the mobility values relevant to the device performance. Based on the extracted $\mu_0$ and $\beta$, we deduced the carrier mobility at the applied electric field of $4.15 \times 10^5 \text{ V/cm}$, corresponding to the field strength in the EL devices under a voltage bias of 5 V (Fig. 2). Notice that the hole mobility decreases monotonically with the decrease in the compositional fraction of NPB ($C_N$), while the electron mobility approximately decreases with the decrease in $C_N$ and reaches the minimum as $C_N=25\%$. Although the behaviors above were similarly observed in other mixed polymer systems, our experimental results represent the charge mobility measurement on the mixed organic semiconductor system based on small molecules. The two behaviors above can be understood qualitatively based on the following three facts. First, the highest occupied molecular orbital energy level of NPB is at 5.4 eV with respect to the vacuum level and that of Alq3 is at 5.8 eV. In the mixed NPB-Alq3 system, the Alq3 molecules therefore act as “blocking hills” to the hole conduction pathways in the connected networks made by NPB molecules. Second, the lowest unoccupied molecular orbital energy level of Alq3 is at 3 eV relative to the vacuum level and that of NPB is at 2.4 eV. In the mixed system, the Alq3 molecules therefore act as “traps” to the electron conduction pathways in the connected networks made by NPB molecules. Third, the constituted charge mobility is dependent on the relative charge (hole or electron) mobility of composing NPB and Alq3. Since the electron mobility of NPB is comparable to that of Alq3, the electron mobility thus decreases initially with $C_N$. After the percentage of NPB molecules reaches more than 25%, the connected networks of NPB molecules are formed to facilitate the electron transport, leading to the observed increase in the electron mobility with $C_N$. In contrast, since the hole mobility of NPB is much larger than that of Alq3, the increase of the percentage of Alq3 creates more blocking hills for the hole transport and thus makes the resultant hole mobility smaller. Most recently, Fischchuk et al. have derived a non dispersive hopping charge transport model based on effective-medium theory in which the hopping events between identical and different molecules in the mixed system have been taken into account with the consideration of wave-function overlapping integral between the hopping sites and the energy level difference between them. According to this model, the sensitive dependence of charge mobility on the compositional ratio is predicted and a critical compositional ratio exists for minimum mobility, agreeing qualitatively with the observed behaviors in this study. We note that Aziz et al. proposed that the transport of holes into Alq3 may create unstable cationic Alq3 species, leading a decrease in device performance. This finding suggests that the mobility of hole and electron may also be influenced by the generation of a heretofore unidentified defect site created in the interaction between NPB and Alq3 in mixed layer, although no clear evidence is provided by our absorption and fluorescence spectroscopic measurements. It is therefore possible that the observed relationship between the charge mobility and the compositional fraction is caused by the sensitive dependence of the charge mobility on the very small amount of the defects produced in the mixed organic system.

The systematic study of the dependence of the charge mobilities of the mixed organic films on the compositional fraction thus helps to reveal the $L-J-V$ characteristics and the EL spectra of the OLEDs with a mixed layer. Figure 3 shows the dependence of current density ($J$) on $C_N$ of the mixed layer in the EL devices at a bias voltage of 5 V. The two heterojunction typed devices with the mixed layer replaced by a neat NPB ($C_N=100\%$) or neat Alq3 ($C_N=0\%$) layer are also displayed for comparison. Notice that the two mixed-layer devices with $C_N=50\%$ and 75% have significantly higher current density than that of the mixed-layer device with $C_N=25\%$ which is even lower than that of the two heterojunction typed devices. This abnormal behavior can be understood by the dependences of electron and hole mobili-
ties on the mixing concentration. For $C_N=25\%$, the electron and hole mobilities of the mixed layer are considerably smaller than those with the other two mixing ratios, thus resulting in the smallest current density. It is even smaller than that with $C_N=0\%$. This is reasonable because although the hole mobility of neat Alq$_3$ is much smaller than the mixing one with $C_N=25\%$, it is compensated by the much higher electron mobility of the neat Alq$_3$. These results indicate that the charge transport behavior of the EL devices with a mixed laser is greatly influenced by the difference between the energy levels and the carrier mobility of the mixed layer, which may alter the exciton recombination regime of these devices. Because there is no clear junction between the ETL or HTL layer, the electrons (holes) can then jump between adjacent Alq$_3$ (NPB) molecules when they move from the ETL (HTL) to the mixed layer. The electron and hole distributions can then be extended into the mixed layer in which the excitons are formed, resulting in a broad recombination regime. This is in great contrast to the HJ devices where the recombination regime is located at the heterojunction interface. The variation of the recombination regime is reflected by the EL spectra of these devices, as shown in Fig. 4(a). Note that the peak wavelength of the EL spectrum is blueshifted with the NPB volume fraction $C_N$. According to the optical interference effect in the optical cavity structure of our OLED devices, the observed blue-shifting behavior indicates that the center for the recombination is gradually moved from the HTL-ETL junction into the mixed layer. Furthermore, Fig. 4(b) shows the luminescence efficiency as a function of the current density of the mixed-layer devices. The luminance efficiency is represented by $L/J_A$, where $J_A=1-C_N$ and is the compositional fraction of Alq$_3$. Notice that the efficiency decreases with $C_N$. Due to the fact that the hole mobility of NPB is much higher than the electron mobility of Alq$_3$, it is expected that the smaller $C_N$ is, the more excitons are formed in the mixed layer, preventing electrons and holes from piling up and thus creating higher probability for the exciton formation. The device modeling considering the mixed layer is under way for more detailed investigation of the complete device performance.

In summary, we have determined the charge drift mobility of the organic thin film samples of neat NPB and Alq$_3$ layers, and three mixed NPB-Alq$_3$ layers ($C_N=75\%$, 50\%, and 25\%). The dependence of the charge mobility at the device operating voltage bias on the compositional fraction has been deduced to interpret the EL spectra and $L-J-V$ characteristics of the heterojunction and the mixed-layer devices. The results of the EL spectra indicate that the recombination regime of the mixed-layer devices is located in the mixed layer and depends sensitively on the compositional fraction in the mixed layer. The conclusion above is consistent with the luminance efficiency result. This study thus presents the direct evidences on the role of the mixed layer in the device performance and provides guidelines in optimizing the OLED structure.