Estimation of electron mobility of n-doped 4, 7-diphenyl-1, 10-phenanthroline using space-charge-limited currents*

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Abstract: The electron mobilities of 4, 7-diphenyl-1, 10-phenanthroline (BPhen) doped 8-hydroxyquinolinato-lithium (Liq) at various thicknesses (50–300 nm) have been estimated by using space-charge-limited current measurements. It is observed that the electron mobility of 33 wt% Liq doped BPhen approaches its true value when the thickness is more than 200 nm. The electron mobility of 33 wt% Liq doped BPhen at 300 nm is found to be ~5.2 $\times 10^{-3}$ cm²/(V·s) (at 0.3 MV/cm) with weak dependence on electric field, which is about one order of magnitude higher than that of pristine BPhen (3.4×10^{-4} cm²/(V·s)) measured by SCLC. For the typical thickness of organic light-emitting devices, the electron mobility of doped BPhen is also investigated.

1. Introduction

Since the fabrication of the first successful organic light-emitting diodes (OLEDs) by Tang and Van Slyke[1, 2], good steady progress has been made in improving these devices for use in practical applications. The power consumption and reliability of OLEDs have been key issues for real applications and have shown remarkable progress through intensive research in the past decade[3−5]. The device performances have been significantly improved to meet commercial demands. However, power consumption and reliability for flat panel displays are not satisfactory yet. One of the most effective solutions for the requirements can be an improvement of the luminous efficiency of OLEDs. The charge balancing of the electron and hole in the recombination zone is crucial to improve the luminance efficiency and the stability of an OLED[6, 7]. Therefore, mobility evaluation for amorphous organic semiconductors is very important to the development of OLED technology. The time-of-flight (TOF) technique has been widely used for the mobility measurement of organic materials used in OLEDs[8]. For mobility measurements in the TOF technique, the transient photocurrent is monitored as charge carrier drift to the charge-collecting electrode under an applied voltage after a pulsed laser illuminates the sample. However, the electrical signal is usually small due to the low density of charge carriers generated by laser light and thus results in a low signal-to-noise ratio. For this reason, the thickness of the organic layer for TOF measurement is around 2–8 μm. The thickness of the organic layer is much thicker than the typical value of 50–100 nm in OLEDs. Therefore, the mobility data from TOF measurements may not be directly applicable in performance simulation or device design because the mobility is thickness dependent. The time-delay measurement of the transient electroluminescence (E) signal is another method of evaluating the mobility of organic semiconductor. It has been used to determine the electron mobility of Alq₃ for thicknesses from 60 to 250 nm in typical double-layered devices[9].

Space-charge-limited (SCLC) measurements have also been used to evaluate carrier mobility under a steady current state in an organic layer[10, 11]. Yasuda *et al.* reported the electron mobilities of several electron transporting materials estimated by the steady-state SCLC[12]. Although the SCLC theory is well established, mobility analyses of organic semiconductors have rarely been used. The reason for this is that the key requirement of SCLC for mobility measurements is a good ohmic (or quasi-ohmic) contact between the organic layer and the metal electrode. A proper buffer layer showing quasi-ohmic contacts for the charge injection makes it possible to utilize the SCLC for mobility measurements[12, 13]. Chu *et al.* reported that the electron mobility of Alq₃ estimated by field-dependent SCLC by introducing a quasi-ohmic contact of LiF was found to be 5.2×10^{-6} cm²/(V·s) (at 0.8 MV/cm)[14]. This result is in good agreement with the value estimated by TOF[15]. One of our group reported the electron mobility of pristine BPhen (4, 7-diphenyl-1, 10-phenanthroline) using SCLC theory with a quasi-ohmic contact of LiF, which was found to be 3.4×10^{-4} cm²/(V·s) (at 0.3 MV/cm)[16]. This result is also in good agreement with the TOF[17]. However, stud-

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ies describing the electron mobility of doped organic semiconductors (Liq-doped BPhen) using SCLC theory have not yet been reported.

In this letter, we have applied the SCLC method to evaluate the electron mobility of an electron transporting material (BPhen) doped with 8-hydroxyquinolinato-lithium (Liq). For the electron mobility measurements of BPhen doped [33wt% Liq], lithium fluoride (LiF) was used as a buffer layer between the organic layer and the Al electrode because it significantly enhances the electron injection by effectively reducing the electron injection barrier[18, 19] between the Al electrode and the organic layer. Therefore, we can say that electron conduction in our devices is not limited by injection. The electron mobility of Liq-doped BPhen at various thicknesses (50–300 nm) has been determined by SCLC measurements. The electron mobility of doped BPhen with a thickness of 300 nm is estimated to be ~5.4×10^{-3} cm^2/(V·s) (at 0.3 MV/cm), which is about ten times greater than that of pristine BPhen (3.4×10^{-4} cm^2/(V·s)) measured by SCLC[16]. The estimated electron mobility of doped BPhen in a typical OLED thickness in this work would be very meaningful because the electron mobility of organic materials in this region cannot be measured by TOF.

2. Experiment

Indium tin oxide (ITO) was used as an anode electrode. Glass coated with indium tin oxide (ITO) was used as a starting substrate. ITO was then cleaned with detergent and sprayed with de-ionized (DI) water. ITO was further cleaned ultrasonically for at least 10 min. After drying it in an oven for 30 min, it was treated by UV ozone. The n-doping layer [BPhen: x% Liq] was co-deposited and devices were prepared by vacuum vapor deposition (1.0×10^{-6} torr) onto an indium tin oxide coated glass substrate with a sheet resistance of 20 Ω/. The typical device structure was ITO/[BPhen: 33wt% Liq (50, 100,150, 200, and 300 nm)]/LiF(1 nm)/Al(150 nm).

The deposition rate for the organic layer was 2–3 Å/s while that of LiF and Al was 0.1 and 20 Å/s, respectively. The active area of the devices was 5×5 mm^2. The thickness of the layers was monitored by using a quartz-crystal monitor. The current–voltage (I–V) characteristics were measured by a computer controlled programmable Keithley 2400 dc source meter.

3. Results and discussion

Figure 1 shows the current density–voltage (J–V) characteristics of doped BPhen at various concentrations of Liq. A dramatic increase in the current density and considerable reduction in the voltage were observed when Liq was doped into BPhen. It can be seen that the current density increases with increasing concentration of Liq into BPhen and then decreases when the concentration of Liq reaches 50wt%. In this way, we obtained the optimal concentration of Liq into BPhen, which
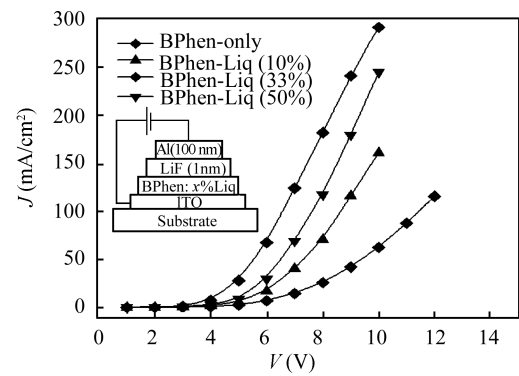

Fig. 1. Current density versus voltage (J–V) characteristics of electron-only devices at various concentrations of Liq. Inset shows schematic structure of electron-only devices.

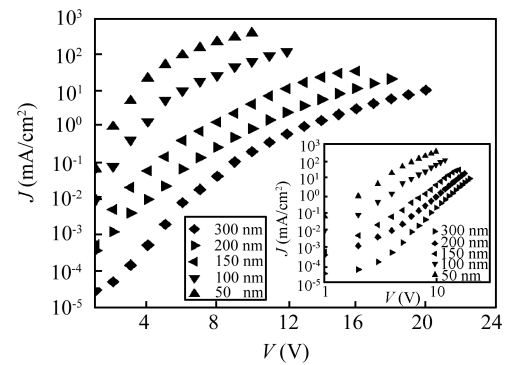

Fig. 2. Current density versus voltage (J–V) characteristics of electron-only devices at various thicknesses of BPhen doped Liq [33wt%]. Inset shows log–log plot between J–V.

is 33wt% Liq[22]. Therefore, we chose 33wt% Liq to measure the electron mobility of the BPhen: Liq layer.

The schematic structure of electron-only devices is shown as an inset in Fig. 1. We fabricated electron-only devices with a structure of ITO/[BPhen: 33wt% Liq(x nm)]/LiF(1 nm)/Al(150 nm), where x = 50, 100, 150, 200 and 300 nm. Moreover, the electron-only[16, 19, 24] devices were prepared without a buffer layer (hole blocking layer) because BPhen itself possesses a large highest occupied molecular orbital (HOMO) and due to its deep HOMO value (6.4 eV)[20, 21] it is not necessary to use an extra thin layer of hole blocker like BCP. Figure 2 shows the current density–voltage (J–V) characteristics at various thicknesses of doped BPhen. The J–V characteristics show two distinct regions at low and high biases, such as the Schottky thermionic region and the SCLC region, respectively. As the voltage increases, the J–V characteristics switch to the SCLC[16] and the SCLC can be expressed as

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{E^2}{L}, \tag{1}$$

where E is the electric field, ε and ε_0 are the relative dielectric constant and the permittivity of the free space, respectively, and L is the thickness of the organic layer. The carrier mobility is affected by energetic disorder due to the interaction of each hopping charge with randomly oriented and randomly located dipoles in the organic thin film[21].
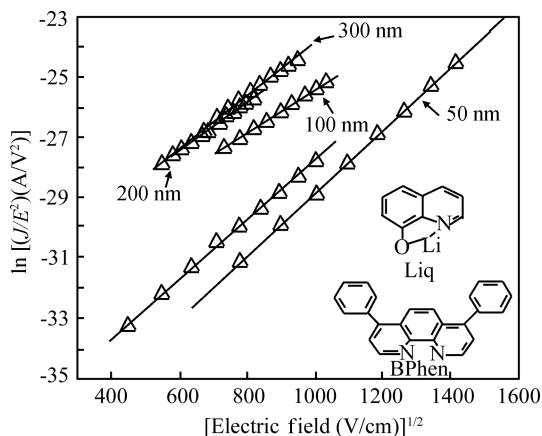
Fig. 3. Space-charge-limited currents for devices at various thicknesses of BPhen:Liq[33wt%]. The solid (black) lines are best fits to the space-charge-limited current behavior. Inset: molecular structure of BPhen and Liq.
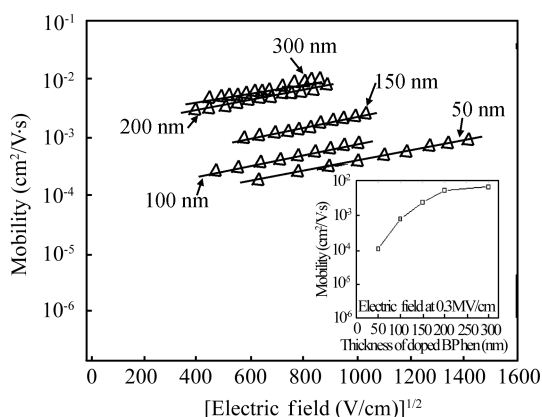

Fig. 4. Mobility-square root of electric field for different thicknesses of BPhen: 33wt% Liq. Inset: Thickness dependence of mobility at an electric field of 0.3 MV/cm.

Therefore, the mobility is dependent on the electric field and can be expressed by a Poole-Frenkel (PF)-like equation,

$$\mu\left(E\right) = \mu_0 \exp\left(\beta \sqrt{E}\right), \qquad (2)$$

where μ_0 is the zero-field mobility and β is the Poole-Frenkel factor. From a combination of Eqs. (1) and (2), the field dependent SCLC can be easily expressed by

$$J = \frac{9}{8}\varepsilon\varepsilon_0 \frac{E^2}{L}\mu_0 \exp\left(\beta \sqrt{E}\right). \qquad (3)$$

Figure 3 shows the logarithm of J/E^2 versus the square root of the mean electric field. The fitted lines are in good agreement with the experimental data and the current in this region follows field-dependent SCLC behavior. The slope and the intercept give β and zero-field mobility (μ_0), respectively. Here, the relative dielectric constant (ε) of organic material is assumed to be $3^{[22-26]}$, and the permittivity of the free space (ε_0) is 8.85×10^{-12} F/m.

Figure 4 shows the field dependence of electron mobility at various thicknesses of BPhen doped Liq, while the inset shows mobility variations with BPhen thickness at an electric field of 0.3 MV/cm. It can be seen that the mobility increases
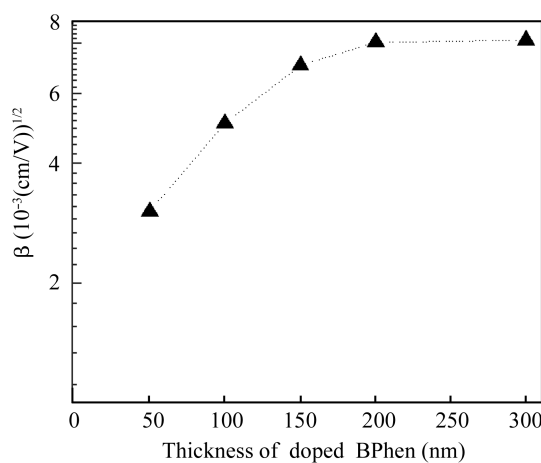

Fig. 5. Dependence of Poole-Frenkel (PF) slope (β) on [BPhen: 33wt% Liq] thicknesses.

with increasing thickness of Liq-doped BPhen and then reaches a saturation value when the thickness of doped BPhen is greater than 150 nm. We can explain this by the fact that, in a thicker film ($x > 150$ nm), the contribution of the interfacial effect to the effective electron mobility of BPhen becomes weaker and bulk properties are predominant, resulting in high electron mobility. As the thickness increases further, the mobility becomes insensitive to thickness change and approaches the value of electron intrinsic mobility of Liq-doped BPhen. For an electric field at 0.3 MV/cm the estimated electron mobility of doped BPhen is $\sim5.2 \times 10^{-3}$ cm^2/(V·s) at 300 nm thickness. This value is ten times greater than the reported value 3.4×10^{-4} cm^2/(V·s) for pristine BPhen from SCLC. However, we need to estimate the practical mobility in OLEDs because the BPhen thickness in a typical OLED device is ~50 nm. When we change the thickness from 50 to 300 nm, the mobility is found to increase roughly ten times from 5.6×10^{-4} cm^2/(V·s) to $\sim 5.4 \times 10^{-3}$ cm^2/(V·s) at 0.3 MV/cm. The thickness dependence of the electron mobility in Alq$_3$ was also observed by transient EL$^{[9, 21]}$. The results showed trends similar to our results in this work. So, we can conclude that SCLC is a promising method for mobility measurement of BPhen doped Liq. Another method, the TOF technique, requires quite thick films of several microns and, in addition, cannot estimate the practical mobility in the typical thickness of about 50 nm in OLED devices.

Figure 5 shows the β values versus various thicknesses of Liq-doped BPhen. It can be seen that β initially increases monotonically with increasing thickness which is in good agreement with the PF plot, i.e., a large β and hence strong field dependence in mobility as thickness increases$^{[9]}$. However, β tends to saturate as thickness $x > 150$ nm, and reaches a saturation value of $\sim8.1 \times 10^{-3}$ (cm/V)$^{1/2}$. From Figs. 4 and 5, we can deduce that for small thicknesses, the computed electron mobility deviates from the intrinsic mobility. Furthermore, the insensitivity of both mobility and β to thicknesses greater than 150 nm is an indication that the estimated mobility is approaching the true values of the intrinsic electron mobility in doped BPhen. However, it has been observed that

the zero-field mobility μ_0 increases from 5.53×10^{-6} to 7.63×10^{-4} cm^2/(V·s) when the thickness of BPhen increases from 50 to 300 nm.

4. Conclusions

In summary, we have demonstrated that the SCLC technique can be used to estimate the electron mobility of a BPhen doped Liq layer. We have found that the doping of Liq into BPhen significantly enhanced the mobility of pristine BPhen. We observed that at higher thicknesses of BPhen doped Liq [33wt%] (i.e., $x > 150$ nm), the mobility became insensitive to the thickness change and approached the value of intrinsic electron mobility of the doped BPhen layer. The investigated electron mobility of Liq-doped BPhen at 300 nm was found to be $\sim 5.2 \times 10^{-3}$ cm^2/(V·s), which is ten times greater than that of pristine BPhen. The electron mobility of doped BPhen at a typical OLED thickness was also estimated by SCLC measurements. We observed that at a typical thickness ($\sim$50 nm) of BPhen: Liq [33wt%], the estimated mobility is $\sim 1.7 \times 10^{-4}$ cm^2/(V·s). These results may be a very useful tool for device design and improvement in the performance of organic light-emitting diodes.

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