Investigating the effect of the conductivity of the electron transportation layer on the organic light-emitting diodes

Jinxiang chen\textsuperscript{1*}, Shipan Wang\textsuperscript{1}, Hang Zhou\textsuperscript{1}
1.Peking University ShenZhen Graduate School University Town, Nanshan District, Shenzhen 518055, P.R.China
Email: chenjinxiang1@tcl.com; Email: zhouh81@pkusz.edu.cn

Abstract. In this paper, we choose three types of n-doped electron transport layer (ETL) materials with different chemical structures to fabricate only-electron carrier device for studying the conductivity of them, namely, 100 nm ETL1, 40 nm ETL2, and 23 nm ETL3. It is also analyzed that the effect of the potential barrier height on the carrier injection efficiency of the single-carrier device when they directly contact with the electrode having the different work function ITO (indium tin oxide film) electrode. When the thickness of the organic electron transport layer is thin, the current density is mainly limited by the injection barrier in the interface, However, When the thickness of the organic electron transport layer is thick, the organic electron transport layer with very low carrier mobility is a dominant factor in limiting the current through the device. If ETL1 is in contact with a lower work function aluminum electrode relative to the ITO electrode, the effect of the injection limit on the current is weaker. Considering Poole-Frenkel effect and space charge limited current effect, the field strength-dependent carrier mobility of ETL1 material is estimated by linear-fitting the current-electric field characteristic curve of only-electron device. Organic red light-emitting diode is fabricated with ETL1 thicknesses of 10 nm and 100 nm, respectively. For the organic light-emitting device with 100 nm ETL1, it reaches 14.9 cd/A at a current density of 30 mA/cm\textsuperscript{2}, and the color coordinates is (0.658, 0.341).

1. Introduction

Organic light-emitting diodes(OLED) have been widely used in the fields of illumination, panel display, etc., and organic semiconductors(OS) are sandwiched between the different work function electrode to form the basic device frame of OLED.[1] In order to improve the turn-on voltage and luminous efficiency, except for the proper selection of the metal electrode, an interface modifying layer is introduced between the electrode and the organic layer.[2] The later one is a common method that works well. It is well known that the closer the work function of the electrode is to the Fermi level of the semiconductor, the lower the injection barrier can is, so the turn-on voltage of the OLED will be decreased and the luminous efficiency could be increased. Here, a single carrier device are fabricated using these ETL materials having different chemical structures. The effect of the potential barrier from the direct contact between the high work function electrode and the organic semiconductor electron transport layer(ETL) on the carrier transportation will be analyzed from the measured current-electric field (J-E) characteristic curve.

By comparing the J-E curves at forward voltages bias with that at negative voltage bias, we can get some information about the interface barrier height. The thickness of ETL is comparable to that...
of the real OLED device. Actually, the thickness of the thickness of ETL is intensively related to the current density through the whole device. If the contact interface is an ideal ohmic contact, the material bulk-resistance is dominant in limiting current density.\textsuperscript{[3]} In this paper, the luminous efficiency of the OLED is experimentally proved to be improved by adjusting the thickness of the ETL.

The ETL material widely used is usually disordered amorphous hydrogen-carbon materials, and the electronic state of such materials is the localized state disorderly.\textsuperscript{[4]} Almost, all carriers are localized, there are no real free carriers, the migration of most of free electrons in organic semiconductor materials is limited by high-density trap state, and the energy levels of the trap for the organic semiconductor are similar, so most of which are essentially a p-type semiconductor with the hole mobility greater than the electron mobility.\textsuperscript{[5]} However, although the carrier concentration of the ETL is generally relatively low, the conductivity can be significantly improved by doping a certain amount of electron donor material as an additive.\textsuperscript{[6]}

Firstly, it is well known that the carrier mobility of most OS exhibits an electric field dependency. But, here, we introduce a constant factor H, that can be expressed by the Poole-Frenkel(P-F) equation

$$\mu(E) = \mu_0 e^{\beta/\epsilon r}$$  \hspace{1cm} (1)

$\mu_0$ is the zero field mobility and $\beta$ is the poole-frenkel factor.

The no-trap space charge limited current

$$J = \frac{q}{8} \epsilon r \epsilon_0 \frac{E^2}{L}$$  \hspace{1cm} (2)

$J$ is the current density, $E$ is the electric field, $L$ is the thickness of the film, $\epsilon r$ is relative dielectric constant and $\epsilon_0$ is vacuum dielectric constant. and so

$$J = \frac{9}{8} \epsilon r \epsilon_0 \frac{E^2}{L} H \mu_0 e^{\beta/\epsilon r}$$  \hspace{1cm} (3)

It can also be rewritten as

$$\ln \frac{J}{E^2} = \ln \left( \frac{9}{8} \epsilon r \epsilon_0 \frac{H \mu_0}{L} \right) + \beta \sqrt{E}$$  \hspace{1cm} (4)

The deduced formula includes the information that the carrier mobility of the material is a function of the electric field strength.\textsuperscript{[7]}

The conductivity of metal materials well obeys Ohm’s law. However, for insulators, low carrier mobility semiconductors, and organic materials with generally high trap densities, current-voltage characteristics is often studied using the P-F effect. The P-F emission effectively explains the phenomenon that as the electric field strength increases, the conductivity of such materials increases. For the low carrier mobility for organic semiconductor materials, under the high-intensity electric field, the internal potential well is lowered to cause the restricted carriers to escape, increasing its conductivity. The formula is as follow.

$$J = C E e^{\left[ \frac{\mu B}{q \epsilon r \epsilon_0 \sqrt{E}} \right]}$$  \hspace{1cm} (5)

Where $\varphi_B$ is the barrier height, $q$ is the unit charge, and $\epsilon r$ is the relative dielectric constant. $C$ is constant factor, $k$ is Boltzmann constant.

When the Poole-Frenkel\textsuperscript{(P-F)} effect becomes the dominant mechanism of conduction current, $\ln(J/E)$ and $\sqrt{E}$ should be linear.\textsuperscript{[8]}

### 2. Experiment

In order to investigate the conductivity of the n-doped electron transport layer, a single electron device was prepared. The structure of a single carrier device is shown in Figure 1. Patterned indium tin oxide (ITO)-coated glass with a sheet resistance is cleaned by ultrasonic in deionized water. The thicknesses of ETL1, ETL2, and ETL3 are 100 nm, 40 nm, and 23 nm, respectively. The devices in Figure 1 (a), (b), (c) are respectively named device A, device B and device C. The ETL by the thermal evaporation covers the ITO anode or the ITO/Al anode. The current density–voltage ($J$–$V$) characteristics is recorded with a Keithley 2400 source unit. This paper analyzes the $J$–$V$ curve under the
external electric field by simulation in order to extract the electrical properties of the ETL such as mobility, dielectric constant and so on.

Figure 1. the device structure of the diode based on the ETL doping with Liq. (a), (b), (c) respectively represents the device A, the device B and the device C. (d) represents the improved structure of ETL1 device, named as device D.

3. References

Figure 2 shows the current density–field (J-E) intensity characteristics of a single-carrier device made by different ETL materials under the forward and negative electric field. The ITO electrode is regard as the positive electrode, reversely, the Ag electrode is the negative electrode. Both device A and device B show bidirectional conductivity. Likely, there is an electron injection layer (EIL) between the ITO electrode and the ETL. The device C is only positively conductive. To some extent, this indicates that large contact potential barrier is formed between ETL3 and the ITO electrode. In general, its Fermi level of the n-type doped ETL can rise above the forbidden band, near the Lowest Unoccupied Molecular Orbital (LUMO) conduction band. In result, there is a very large contact barrier when it directly contacts with the high work function ITO electrode. However, the potential barrier varies with the applied external electric field, the potential barrier will be weakened or enhanced. The applied forward voltage will lower the potential barrier, and the reverse voltage will make the barrier increases, which is how the rectifier diode works. In the ETL3 device structure, the J-E characteristic clearly shows the rectification characteristics that the forward current is significantly larger than the reverse current.

Figure 2. the J-E characteristic curve of the diode device with ITO electrode or ITO/Al electrode.
For the device A, the ETL reaches 100 nm, the electric field intensity scanned from -1 MV/cm to +1 MV/cm. When the electric field strength is +1 MV/cm, the current density is $6.4 \times 10^{-3}$ A/cm$^2$, then, the electric field strength in the negative direction is -1 MV/cm, and the current density is close to the forward current density, which is $6.8 \times 10^{-3}$ A/cm$^2$. For the device A, the thickness of the ETL2 material is only 40 nm. When the electric field strength reaches +1 MV/cm, the current density is only $4.64 \times 10^{-4}$ A/cm$^2$. Such low current density means that the limiting-current factor is not only the material bulk-resistance but the interface potential barrier.

We further apply the space charge-limited current model (SCLC) and the P-Femission model to analyze the current density of the device A.

The scan voltage applied to the device A changes from negative bias to positive bias, we get the current density-field intensity curve. Interestingly, it is noticeable that the current density is not minimum under the zero-electric filed. Importantly, there is already a certain amount of space charge accumulation inside the device, so, if the current under the forward voltage is analyzed, the effect of space charge on conductivity should be considered. At the same time, for a 100 nm thick ETL material, the field-dependent mobility is not negligible.

Figure 3(a) shows the calculated data used for linearly fitting with Equation (3). The result is as follow.

$$Y=0.0114X-43.677$$

(6)

$Y$ is the vertical coordinate, $X$ is the horizontal coordinate.

Here, the intercept is -43.677. Based on the latter information in this paper, we order that the relative dielectric constant is 3.6, so, the $\varepsilon_0 \mu_0$ is $2.99 \times 10^{-12}$ cm$^2$/V$^2$s$^{-1}$, where the Poole-Frenkel factor is 0.0114. Substituting them into Equation (1), Figure 3 (b) shows the carrier mobility as a function of electric field strength.

Figure 3. (a) The $\ln(J/E^{1/2})$ versus $E^{1/2}$ curve characteristic of ITO/ETL1/Ag device applied with positive voltage bias. (b) Carrier mobility $\mu$ versus electric field intensity $E$ curve characteristic of ITO/ETL1/Ag device. (c) $\ln(J/E)$ versus $E^{1/2}$ curve characteristic of ITO/ETL1/Ag device applied with negative voltage bias. (d) $\ln(E)$ as a function of $\ln(J)$ for the analysis of the SCLC.

At the start of scanning, the negative electric field is applied to the fresh device A with no current through it ever, the current-voltage characteristic curve is obtained. It is necessary to consider that both the interface contact potential barrier and the P-F effect influence the conductivity. Based on the previous report, The current density as function of the field intensity is fitted using Equation (5). The result is as follow.
It is approximately inferred that the relative dielectric constant of the ETL1 material is 3.63, which is in the range of the dielectric constant of the common ETL. It can also be calculated that the height of the barrier is 0.818 V, which is lower than the expected value. It may be that the EIL layer lowers the barrier potential height.

In order to further explore the influence of the interface barrier height on the current-voltage characteristics, the structure of the ETL1 device is improved, and the lower work function metal Aluminium (Al) was vacuum thermal-evaporation deposited on the ITO electrode. According to the literature, the work function of the Al is 4.2 eV, which is lower than that of ITO. The work function of the ITO is 4.7 eV, and the J-E characteristic curve is obtained as shown in Fig. 2 (d). Compared with the pure ITO electrode, the current density is greatly improved under the same electric field strength. When the electric field intensity reaches 0.5 MV/cm, the current density reaches 5.92 A/cm², much larger than that of pure ITO electrode which is 4.729 × 10⁻⁵ A/cm². This means that the lower work function metal Al electrode is more conductive.

The double-logarithm of the J-E characteristic curves under the forward electric field is shown in Fig. 3(d), we find that when the electric field strength increases to 0.32 MV/cm, the space charge limiting current (SCLC) region gradually appears.

Using the formula (2) to analyze the SCLC from the J-E, we get the following linear formula

\[ Y = 0.0146 \times X - 30.019 \]  

(7)

\[ Y=2.0439 \times X-25.109 \]  

(8)

From the above formula, the carrier mobility is 3.47×10⁻⁴ cm²/V·s⁻¹, and it can be seen that the electron mobility is greatly improved after ETL1 n-type doping. So, when the electric field intensity is 0.32 MV/cm, the carrier mobility 3.47×10⁻⁴ cm²/V·s⁻¹. During the SCLC process, the mobility is seen as be constant. Lastly, we calculate the H value is 5.46 ×10⁻⁶. The reason why the value is greatly low is unknown. The zero-field mobility is 5.49×10⁻⁷ cm²/V·s⁻¹.

Intriguingly, red-light OLED devices are prepared using a 10 nm ETL1 film and a 100 nm ETL1 thick film. At around 1000 nits, the color coordinates, the applied voltage, the current density and the current efficiency and luminescence peaks are listed in Table 1. The luminous efficiency of thin ETL1 OLED is apparently higher than that of thick ETL1 material. So, the thickness of ETL is one of the parameters which affect the efficiency of the OLED.

| Thickness (nm) | Luminance (nits) | CIE x | CIE y | Voltage (V) | J (mA/cm²) | CE (cd/A) | Peak (nm) |
|---------------|------------------|-------|-------|-------------|------------|-----------|----------|
| 10            | 1380             | 0.656 | 0.344 | 3.5         | 5.60       | 24.6      | 616      |
| 100           | 1090             | 0.659 | 0.341 | 4.0         | 6.19       | 17.6      | 616      |

The corresponding curve is shown in Fig.4. The red-lighting OLED with 100 nm ETL1 has a current efficiency of 14.9 cd/A at a current density of 30 mA/cm², a colour coordinate (0.658, 0.341), and a power efficiency of 7.82 lm/W. Unfortunately, the current efficiency commonly decreases with the drop of the current density. It can be seen that the peak of the spectrum is at 616 nm, and there is shoulder peak at near 680 nm, it means that there are more than one kind of photoexcitons. As can be seen from Fig. 4(d), the colour coordinates hardly change with the current density.
4. Conclusion

In this paper, the effects of interface contact potential barrier and organic semiconductor bulk material mobility on J-E characteristics of single-carrier devices were studied. Here, we reveal the competition correlation between the contact potential barrier and the bulk-resistance. When the organic film is thin, the current-limiting factor is the interface property. When the ETL material reaches a certain thickness, the limitation of the material bulk-resistance becomes further stronger. Then, comparing the performance of organic light-emitting devices made with two ETL1 thickness, the ETL1 thin film benefits higher luminous efficiency. Single-carrier devices were prepared using n type-doped ETL. The J-E characteristic curves were measured. Considering the Poole-Frenkel effect and the space-charge limiting current effect, the electric field-dependent electron mobility was obtained. The space charge-limited current model was used to fit the J-E curves from the ITO/Al/ETL1/Ag device, and the SCLC electron mobility was determined to be $3.47 \times 10^{-4} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$. So, this is a useful method to evaluate the carrier mobility of the film.

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