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Electron injection property at the organic–metal interface in organic light-emitting devices revealed by current–voltage characteristics

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ABSTRACT

Electron injection and transport are key issues in organic light-emitting devices (OLEDs). In this letter, we successfully demonstrated the electron injection property which is usually characterized by electronic barrier height from aluminum cathode to tris(8-hydroquinoline) aluminum (Alq_3) or 4,7-diphyenyl-1,10-phenanthroline (BPhen) (the most common two electron-transport materials) by current–voltage (*J–V*) characteristics. The electronic barrier height of 0.66 eV at the Alq_3/Al interface and that of 0.10 eV at the Alq_3/LiF/Al interface was obtained, which is in good agreement with the experimental results investigated by ultraviolet photoelectron spectroscopy (UPS) by Mori et al. [Appl. Phys. Lett. 73 (1998) 2763]. The electronic barrier height of 0.83 eV at BPhen/Al interface and that of 0.098 eV at BPhen/Cs_2O/Al interface was also demonstrated for the first time, suggesting Cs_2O is a highly efficient electron-injection material (EIM) for BPhen. We proposed a simple and yet practical approach to estimate the electron-injection barrier-height at the organic–metal interface in OLEDs. The results were further explained by the dipole effect.

1. Introduction

Organic light-emitting devices (OLEDs) have been attracting considerable attention because of their potential application to flat panel displays and lighting devices [1–3]. Typical OLEDs have a transparent electrode indium–tin oxide (ITO) with high work function deposited on glass for anode and have an opaque metal for cathode such as Mg:Ag [1] and LiF/Al [4] from which light is reflected and emitted through the bottom of ITO glass. Due to the low intrinsic carrier concentrations in organic materials, the current–voltage (*J–V*) characteristics are dominantly injection limited. Actually carrier injection and carrier transport are key issues in OLEDs, and studies on them are of great importance both in the fundamental understanding and in improving the performance. *J–V* characteristics of organic-based devices with diodes structures have been investigated using various models of charge injection and transport such as Richardson–Schottky (R–S) thermionic emission, Fowler–Nordheim (F–N) tunneling, and Pool–Frenkel (P–F) and hopping mechanisms [5–7]. Furthermore, due to the fact that electron mobility in electron-transport materials (ETMs) is much lower than hole mobility in typical hole-transport materials (HTMs) such as *N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl) benzidine (NPB), the intensive and detailed study on enhancement of electron injection would be quite meaningful and practical. A successful demonstration has been elucidated by inserting an electron-injection layer (EIL) of LiF between tris(8-hydroquinoline) aluminum (Alq_3) and Al cathode [4]. Recently, 4,7-diphyenyl-1,10-phenanthroline (BPhen), an effective ETM for OLEDs, has been received much attention due to its high mobility of about two orders higher than that of Alq_3.

On the other hand, due to the fact that LiF cannot prevent chemical reaction between Al and Alq_3, consequently increasing the molecular reaction of Al as depicted: $3LiF+Al+3Alq_3 \rightarrow AlF_3+3Li^+Alq_3^-$ [8]. Other inorganic EIMs such as highly active cesium metal [3] and cesium-based compounds (Cs_2CO_3 [9], Cs_2O [10,11] and CsF [12], etc.) have also shown excellent electron-injection properties. Among them, Cs_2O as EIL demonstrated many merits: (1) its superior electron injection ability is independent of the cathode metals [10,11], (2) molecular Cs_2O is better than metallic Cs and LiF for alleviating the problem of diffusion into organic layer which causes nonradiative recombination [2] and (3) Cs_2O decomposed by Cs_2CO_3 can be easily handled in the fabrication process [11]. However, to the best of our knowledge, there are rare reports on the electron injection property which is usually characterized by electron-injection barrier-height across the interface of BPhen/Al and BPhen/Cs_2O/Al. Here, we proposed a simple and yet practical approach to estimate electronic barrier height at organic–metal interface and successfully demonstrated the electron-injection barrier-height for both Alq_3- and BPhen-based devices. The identity of our

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results revealed by J–V characteristics to those measured by ultraviolet photoelectron spectroscopy (UPS) for Alq_3-based device [13] indicated the validity of our prediction and the results were further explained by the dipole effect.

2. Experimental

Glass coated with ITO was used as starting substrate. It was cleaned with detergent and sprayed with de-ionized (DI) water. ITO was further treated by ultrasonic for 10 min and then UV–Ozone for 6 min. Organic layers were deposited by high-vacuum (10^{-6} Torr) thermal evaporation onto an ITO coated glass substrate with a sheet resistance of 20 Ω/□. The deposition rate for organic materials was 1–2 Å/s while that of Al cathode was 10–20 Å/s. A thin film of Cs_2O with a deposition rate of 0.2 Å/s was deposited onto the organic materials by decomposing Cs_2CO_3 according to the following reaction: $Cs_2CO_3 \rightarrow Cs_2O+CO_2\uparrow$ [2,10]. The chemical structures of employed materials are shown in the inset of Fig. 1.

The active area of the devices was $5 \times 5\ mm^2$. The thickness of the layers was monitored by quartz-crystal monitor. The J–V characteristics were measured by computer controlled programmable Keithley 2400 dc Source Meter. All measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

For the study of electron injection ability at the organic–metal interface, a series of electron-only devices were fabricated. The structures of these devices are listed in Table 1. Fig. 1 depicted the J–V characteristics of the theses devices. As shown in Fig. 1, the current densities of devices without EIL (cells E1 and E2) are very low due to the high energy barrier between organic and Al cathode. A dramatic increase in the current density and a considerable reduction in the voltage are observed when an ultrathin EIL is inserted between organic (Alq_3 or BPhen) and Al (cells E3 and E4). A thin BPhen with thickness of 30 nm is incorporated to impede holes to enter the electron-transport layer

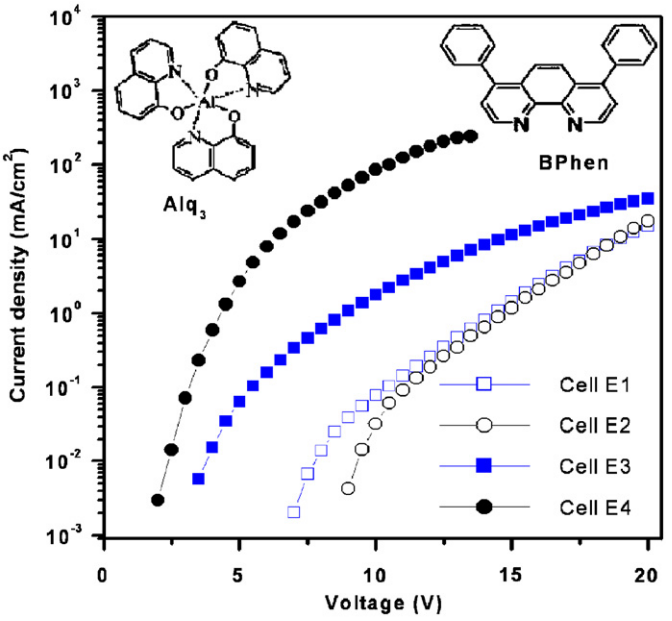

Fig. 1. The J–V characteristics for Alq_3- and BPhen-based devices. The chemical structures of Alq_3 and BPhen are also shown.

Table 1
The structure and the barrier height revealed by J–V characteristics for Alq_3- and BPhen-based devices.

Devices	Structure	Barrier height (eV)[a]
Devices without EIL		
Cell E1	ITO/BPhen(30 nm)/Alq_3(120 nm)/Al(120 nm)	0.66 (0.5)
Cell E2	ITO/BPhen(95 nm)/Al(120 nm)	0.83
EIL-inserted devices		
Cell E3	ITO/BPhen(30 nm)/Alq_3(119 nm)/LiF(1 nm)/Al(120 nm)	0.10 (0.1)
Cell E4	ITO/BPhen(94 nm)/Cs_2O(1 nm)/Al(120 nm)	0.098

[a] The values inside the brackets were derived by Mori et al. [13] using UPS.

(ETL) of Alq_3 in cells E1 and E3, since it possesses a deep highest occupied molecular orbital (HOMO) level of 6.4 eV.

For carrier injection from metals into dielectrics over a Schottky barrier, the J–V characteristics are usually described by the R–S model, expressed by [14]

$$J = A^{*}T^{2} \exp\left[\frac{-q(\Phi_B - \sqrt{qF/4\pi\varepsilon_0\varepsilon_r})}{kT}\right] \quad (1)$$

where J is the current density, A^{*} is Richardson's constant ($A^{*} = 4\pi q m^{*} k^2/h^3 = 120\ A\,cm^{-2}\,K^{-2}$ assuming the effective carrier mass m^{*} equals that of the free electron, h is Planck's constant), Φ_B is the zero-field barrier height, F is the electric filed, ε_0 is the permittivity of free space, ε_r is the relative dielectric constant, k and T are the Boltzmann's constant and ambient temperature, respectively. In Fig. 2 we replot the data shown in Fig. 1 as $\log J$–$F^{1/2}$ plots. It is obvious that devices without EIL (cells E1 and E2) exhibit different field dependence behavior in contrast with EIL-inserted devices (cells E3 and E4). In other words, devices with a thin EIL (cells E3 and E4) do not follow the R–S model, as they show a non-linear dependence of $\log J$ on $F^{1/2}$. For Cell E1 and E2, on the one hand, $\log J$ yields an explicit linear dependence on $F^{1/2}$ as depicted in Fig. 2, indicates an excellent agreement with the prediction of the R–S model. On the other hand, the slope of the fitted straight line is 0.0069 $(cm/V)^{1/2}$ for Alq_3-based device (cell E1) and 0.0060 $(cm/V)^{1/2}$ for BPhen-based device (cell E2), which is a little different from the R–S model-derived value of 0.0085 $(cm/V)^{1/2}$. This can be explained by the fact that the R–S model was developed for high-mobility inorganic materials in which the electronic states are highly delocalized and the conduction is band-type, and thus theoretically it is not fully applicable to the present amorphous material with low mobility. The deviation from the R–S model in Alq_3-based device (Alq_3/Mg:Ag structure) was also observed by Barth et al. [15], although the field dependence resembles that of the R–S model.

Taking into account the charge recombination rate at organic–metal interface, Scott and Malliaras (S–M) have proposed an analytical expression for the net injection current [16]

$$J = 4qN_0\mu F\psi^2 \exp\left(\frac{-\Phi_B}{kT}\right) \exp\left[\frac{q(qF/4\pi\varepsilon_0\varepsilon_r)^{1/2}}{kT}\right] \quad (2)$$

where ψ is a function of the reduced electric field, which is expressed by $\psi(f) = f^{-1}+f^{-1/2}-f^{-1}(1+2f^{1/2})^{1/2}$ with $f = q^3F/\ 4\pi\varepsilon_0\varepsilon_r(kT)^2$, N_0 the density of chargeable sites in the organic material and μ the charge carrier mobility. We tested the data by $\ln(J/F\psi^2)$–$F^{1/2}$ plots, as shown in the inset of Fig. 2, and observed a linear relationship, which is in accordance with S–M model. Furthermore, assuming $N_0 \approx 10^{22}\ cm^{-3}$, $\varepsilon_r \approx 3$, $\mu_{Alq_3} \approx 1\times10^{-6}\ cm^2\,V^{-1}\,s^{-1}$ and $\mu_{BPhen} \approx 1\times10^{-4}\ cm^2\,V^{-1}\,s^{-1}$, based on the present experimental data of the ordinate intercepts of $\ln(J/F\psi^2)$–$F^{1/2}$ and $\log J$–$F^{1/2}$ plots, the barrier heights Φ_B for