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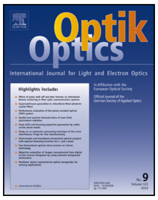

Hole injection engineering with MoO_3 interlayer in organic light-emitting diode revealed by impedance spectroscopy

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ABSTRACT

Inserting MoO_3 interlayer between the indium–tin oxide anode and the most widely used hole transport layer of *N,N*′-bis(naphthalen-1-yl)-*N,N*′-bis(phenyl) benzidine for engineering hole injection in organic light-emitting diode (OLED) is systematically investigated by using impedance spectroscopy. Based on the impedance versus frequency, phase versus frequency, and capacitance versus voltage characteristics, the suitable thickness of MoO_3 interlayer is proven to be less than 30 nm. The suitable thickness of MoO_3 interlayer is further verified by analyzing OLED efficiency. Our investigation indicates that a rather wide range of thickness tolerance of MoO_3 interlayer to great extent facilitates OLED fabrication in practical application.

1. Introduction

Organic light-emitting diodes (OLEDs) have been attracted tremendous attentions due to their potential application in next generation displays and solid state lightings. Typical OLEDs are constructed with a transparent anode of indium-tin oxide (ITO) deposited on glass substrate and an opaque metal cathode of Mg:Ag [1] and LiF/Al [2]. The organic stacks are sandwiched between the anode and cathode. The light is reflected from cathode and emitted through the ITO glass. Achieving high luminous efficiency and low driving voltage are key issues for promoting power conversion efficiency which predominantly determined by carrier injection and transport. Actually, carrier injection and transport are key issues for understanding the fundamentals and boosting device performance.

Generally, the energy barrier between the work function of ITO anode and the highest occupied molecular orbital (HOMO) level of most-widely used hole-transport layer of *N,N*′-bis(naphthalen-1-yl)-*N,N*′-bis(phenyl) benzidine (NPB) is unfavorable for hole injection. Two methods are proposed and extensively investigated with a purpose of softening hole-injection barrier-height: (i) using UV-Ozone, plasma, or chemical treatment for enhancing the work function of ITO anode [3,4]; (ii) sandwiching hole injection layer of PEDOT:PSS [4], $F_{16}CuPc$ [5], PTB7 [6], MoO_3 [7] and graphene [8], etc. The former is usually obtained from other additional equipments, which increases cost and creates contamination. The latter is obtained by thermal deposition under vacuum conditions or using processable spin coating, which is compatible with the state-of-the-art OLED fabrication process. In comparison, MoO_3 is superior to other choices of interface engineering materials and attracts special focus.

Carrier injection evaluation can be explicitly observed through the *I*–*V* measurements [9]. However, the *I*–*V* functions effectively only when a drift current flowing in the device and little information is achieved under reverse bias. X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) are proven to be effectively characterize the energy level alignment and band bending at the interfaces from which the carrier injection ability is revealed [4,10–12]. Recently, impedance spectroscopy has been developed as a useful and robust tool for investigating electrical properties at the interfaces as well as within the organic layers of OLEDs. For instance, the impedance spectroscopy effectively probing the interface engineering [9,13–15], analyzing the distribution of charged carriers [16–18], and detecting the carrier balance [7]. In this study, the hole injection engineering with the extremely important MoO_3 interlayer in OLEDs is revealed. A wide range of thickness

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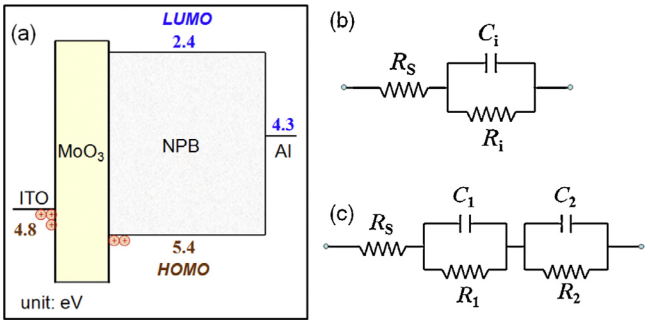

Fig. 1. (a) Schematic structure of HODs. (b) Equivalent circuit of *R*–*CR* for simulating the Cole–Cole plots. (c) Equivalent circuit of *R*–*CR*–*CR* for simulating the Cole–Cole plots.

tolerance of MoO_3 interlayer is deduced from impedance spectroscopy analysis.

2. Experimental details

A series of single carrier device in which holes are extremely predominated (also calls hole only devices, HODs) with a structure of ITO/MoO_3 (0–30 nm)/NPB (80 nm)/Al (200 nm), shown in Fig. 1(a), was fabricated by thermal evaporation under a vacuum of 3×10^{-4} Pa. The ITO coated glass substrate was chemically cleaned and served as anode. The MoO_3 interlayer with different thickness was served as hole-injection layer to align the energy level between ITO and NPB. The NPB was served as the hole transport layer and Al was served as cathode. The device can be considered as a HOD, since a large electron-injection barrier-height of ~2 eV between the lowest unoccupied molecular orbital (LUMO) level of NPB (2.2 eV) and the work function of Al (4.3 eV) effectively impedes electron injecting. The layer thickness and deposition rate of each function layer were monitored *in situ* using an oscillating quartz thickness monitor. The *I*–*V* characteristics and luminance were measured using a Keithley 2400 Source Meter and an L88-OPT Spectra/Luminance Meter. The impedance spectroscopy was measured with a computer controlled programmable Agilent 4294A Precision Impedance Analyzer. All impedance spectroscopy measurements were carried out with amplitude of ac signals of 50 mV.

3. Results and discussions

3.1. HOD without MoO_3 interlayer

Fig. 2 sows the impedance versus frequency (*Z*–*F*) and phase versus frequency (φ–*F*) characteristics of HOD without MoO_3 interlayer (refers as Cell-0). It is clear that Cell-0 shows high impedance of $\sim 10^5\,\Omega$ under sweeping frequency of 40 Hz and zero bias conditions, as shown in Fig. 2(a). The corresponding phase exhibits −90°, as shown in Fig. 2(b). This phenomenon indicates that Cell-0 behaves an insulating state [19]. With the bias voltage increases, the impedance gradually decreases in the range of low frequency (below 10^4 Hz), and the corresponding phase gradually transits from −90° to 0°. It means that carrier injection and transporting occur within the device. On the other hand, the impedance ($\sim 70\,\Omega$ which corresponds to the interfacial resistance R_S probably mostly resulted from the bulk resistance of ITO anode [20,21]) is independent of bias voltage under higher frequency of >10^5 Hz, as shown in Fig. 2(a).

Table 1
Parameters used to simulate the measured Cole–Cole plots of Cell-0.

Bias (V)	R_S (Ω)	C_i (nF)	R_i (Ω)
0	69.01	13.29	2.987E7
2	68.67	13.28	1.618E6
4	68.95	13.23	1.098E5
6	68.74	13.27	2.03E4
8	68.48	13.04	8990
10	68.84	12.75	2926

To further clarify the effect of bias voltage, we delineate the Cole–Cole plots of the complex impedance under different positive bias voltage, as shown in Fig. 3. Here, the frequency increases from right to left for the measured data, and the horizontal and vertical axes of the plots represent the real part *Re*(*Z*) and imaginary part *Im*(*Z*) of the complex impedance, respectively. Under each positive bias voltage, the Cole–Cole plot of impedance resembles a single semi-circle in continuously sweeping frequency. In Cell-0 with sandwich structure, an equivalent circuit, shown in Fig. 1(b), composed of an interfacial series resistor R_S and a parallel circuit connected in series (*R*–*CR*) is commonly used [13,16]. The organic layer of NPB can be simplified as a parallel circuit consists of a capacitor (C_i) and a resistor (R_i). As shown in Fig. 3, by carefully adjusting the parameters (R_S, C_i and R_i), each curve in the Cole–Cole plot can be well reproduced by using the equivalent circuit shown in Fig. 1(b). Table 1 shows the optimized parameters (R_S, C_i and R_i) for fitting the curves under different bias voltage. It can be seen that the capacitance (C_i) almost remains constant (~13 nF) while the resistance (R_i) drastically drops with increasing bias voltage. This makes sense that more charged carriers injected into the device, and the resistor R_i mostly resulted from the NPB layer is considerably decreased with raising bias voltage. The maximum *Re*(*Z*) at ultrahigh frequency corresponds to the interfacial impedance R_S ($\sim 70\,\Omega$) which is independent of bias voltage. While the maximum *Re*(*Z*) at low frequency corresponds to the sum of R_S and R_i (which is strongly bias dependent) (Table 1).

3.2. HODs with different MoO_3 thickness

The *Z*–*F* and φ–*F* characteristics of HODs with 3-nm, 10-nm, and 20-nm thick MoO_3 interlayer (refer as Cell-3, Cell-10, and Cell-20, respectively) show similar characteristics. Taking Cell-20 into

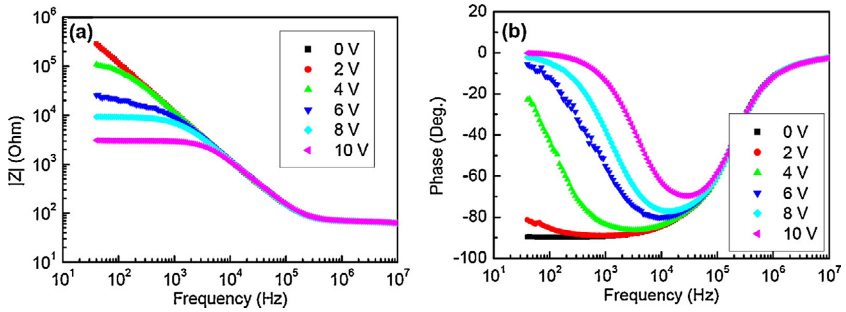

Fig. 2. (a) *Z*–*F* and (b) φ–*F* characteristics of Cell-0.