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Highly enhanced electron injection in organic light-emitting diodes with an n-type semiconducting MnO_2 layer

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ABSTRACT

Highly enhanced electron injection is demonstrated with a thin manganese dioxide (MnO_2) electron injection layer (EIL) in Alq_3-based organic light-emitting diodes. Insertion of the MnO_2 EIL between the Al cathode and Alq_3 results in highly improved device characteristics. *In situ* photoelectron spectroscopy shows remarkable reduction of the electron injection barrier without significant chemical reactions between Alq_3 and MnO_2, which could induce Alq_3 destruction. The reduction of the electron injection barrier is due to the n-type doping effect, and the lack of strong interfacial reaction is advantageous with regards to more efficient electron injection than a conventional LiF EIL. These properties render the MnO_2, a potential EIL.

1. Introduction

Organic light-emitting diodes (OLEDs) have been remarkably attractive for the last two decades due to their unique advantages, such as simple fabrication processes, wide viewing angles, light weight, and mechanical flexibility [1]. However, high charge-injection barrier from the electrode to organic semiconducting materials is one of the inveterate obstacles to design highly efficient OLEDs. Lowering the electron injection barrier in OLEDs especially is a prerequisite to balancing electrons with holes within an emission layer to maximize light emission because most organic semiconducting materials have lower electron mobility than that of hole. It has been reported that the insertion of an appropriate electron injection layer (EIL) reduces the electron injection barrier efficiently. Alkali metals and alkali metal halides have been used as a conventional EIL through the n-type doping effect on an electron transport layer (ETL), such as Alq_3 [2,3]. However, alkali metals are not tractable as an evaporation source and are destructively reactive to the organic molecules. On the other hand, alkali metal halides often show variable performance depending upon the cathode choice [4]. Recently, several alternative EILs, such as alkali metal carbonates, nitride and quinolates [5–11] have been studied and show good electron injection performances. Metal oxides such as ZnO, TiO_2 and ZrO_2 are also candidates for alternative EILs [12–14]. Recently, Luo et al. reported highly efficient OLEDs with insulating manganese monoxide (MnO) EIL [15]. However, its detailed working mechanism is not yet understood. Furthermore, the semiconducting phase of metal oxide would be more suitable for device performance than the insulating phase.

In this paper, we propose that semiconducting manganese dioxide (MnO_2) could be a potential candidate as a

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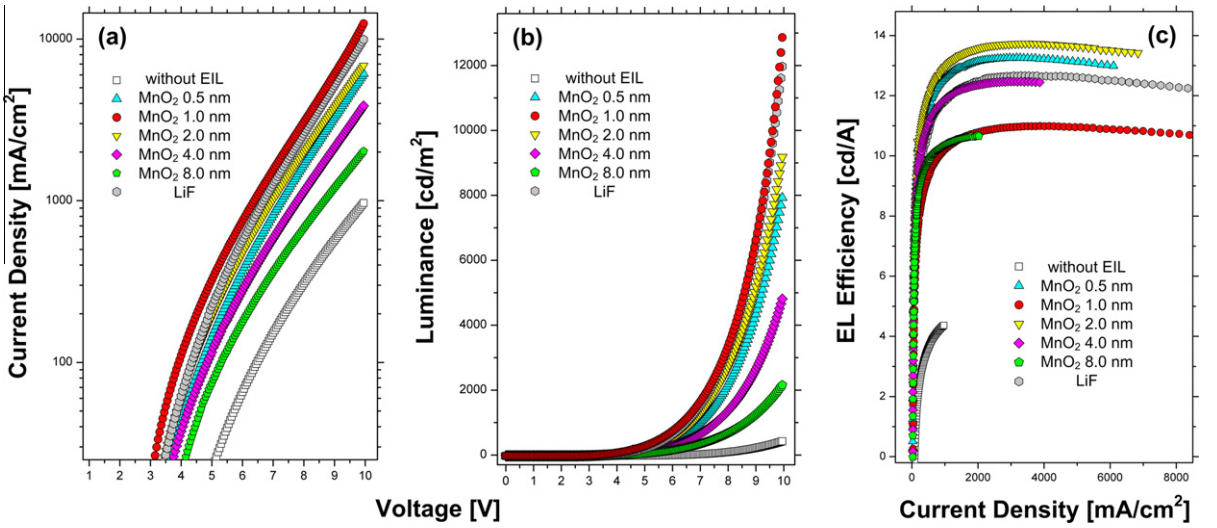

Fig. 1. Measured (a) current density–voltage, (b) luminance–voltage characteristics and (c) EL efficiency of OLEDs with different thicknesses (0, 0.5, 1.0, 2.0, 4.0 and 8.0 nm) of an MnO_2 electron injection layer. The device characteristics with a conventional LiF EIL are also depicted to show the superiority of a MnO_2 EIL.

highly efficient EIL. First, we observed conspicuous enhancements of electron injections with a MnO_2 EIL through OLEDs fabrication including current density–voltage–luminance (*J–V–L*) measurements. We also discovered the optimum thickness of a MnO_2 layer and compared that with a conventional LiF EIL. To elucidate the origin of the electron injection enhancements, we carried out *in situ* photoelectron spectroscopy (PES) experiments. This allowed us to understand the interfacial electronic structures and chemistry which play a crucial role in device performance.

2. Experimental

We fabricated OLEDs with the structure of Al (100 nm)/MnO_2 (0, 0.5, 1.0, 2.0, 4.0, 8.0 nm)/Alq_3 (50 nm)/NPB (50 nm)/ITO. Organic materials and MnO_2 (Sigma Aldrich, 99.99+%) were successively deposited onto the ITO patterned glass substrate by thermal evaporation in an ultra-high vacuum (UHV) chamber below 5×10^{-8} and 2×10^{-7} Torr at the rates of 0.1 nm/s and 0.01 nm/s, respectively. Devices were then completed by depositing the Al cathode on the sample with the rate of >0.1 nm/s. All the deposition rates and thicknesses were monitored by a quartz crystal microbalance. Active areas of the devices are 0.04 cm^2. *J–V–L* characteristics were measured under a dry nitrogen atmosphere using a Keithely 237 and 2400 source measure unit with a photodiode calibrated by a PR650 spectrophotometer. To show the superior electron injection of MnO_2 EIL, OLED with LiF EIL is also fabricated with its optimized thickness (0.1 nm) in our preparation condition.

In situ PES experiments were performed using a PSP RESOLVE 120 spectrometer in an analysis chamber which is directly connected with a preparation chamber. An ultraviolet (He I, 21.22 eV) and a non-monochromatized X-ray (Mg Kα, 1253.6 eV) radiations were used as excitation light sources. To obtain the secondary electron cutoff (SEC), a sample bias of −10 V was applied in normal emission geometry. We used the same interface formation to that of device fabrication because the electronic structures are significantly varied by their deposition sequence between organic and metal electrode [16]. To investigate the effects of the MnO_2 layer insertion, we prepared Al/Alq_3 and Al/MnO_2/Alq_3 samples and compared their electronic structures. In both cases, ITO coated glasses were used as substrates after checking if they all had the same work function. The analysis and preparation chamber were maintained at pressures of 3×10^{-9} and 2×10^{-7} Torr, respectively. The deposition rates were cross checked by a calibrated thickness monitor and by the attenuation of core level intensities in X-ray photoelectron spectroscopy. The interfacial electronic structures of Al/LiF/Alq_3 were referred from well-known reports [4,17].

3. Results and discussion

Fig. 1a and b depicts measured *J–V–L* characteristics. Device performances were highly improved by the insertion of the MnO_2 layer. The optimized thickness of a MnO_2 layer was observed at 1.0 nm and device performance decreased gradually as the MnO_2 layer thickened due to incremental series resistance. However, the device with a relatively thick MnO_2 layer (8.0 nm) still showed better performance than the reference device without MnO_2 insertion. This thickness-independent stability in the device performance originates from the semiconducting nature of MnO_2, which is clear contrast to common EILs such as insulating alkali metal halides [18,19]. As the MnO_2 layer of 1.0 nm is inserted, both current density and luminance increase by more than one order of magnitude at 10 V compared to those of the reference device. Turn on voltage, which is defined as the voltage giving 1 cd/m^2 luminance, was also significantly reduced from 6.4 V to