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Photoemission spectroscopy study on interfacial energy level alignments in tandem organic light-emitting diodes

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ABSTRACT

Organic light-emitting diodes (OLEDs) using a tandem structure offer a highly attractive option for the applications of next-generation flat panel displays and solid-state lighting due to the extremely high brightness and efficiency along with the long operational lifetime. In general, reliable information about interface energetics of the charge generation layers (CGLs), which plays the central role in charge generation and carrier injection into the stacked emission units, is highly desirable and advantageous for interface engineering and the performance optimization of tandem OLEDs. In this review, our recent studies on tandem OLEDs are overviewed, especially from interface energetics perspective via photoemission spectroscopy. The electronic structures of various transition metal oxide (TMO)-based CGLs and their role in charge generation process are reviewed, addressing the n-type doping impact of organic layers in CGLs, thermal annealing-induced oxygen vacancy in TMOs, and the interfacial stability of CGLs on the device operational lifetime. The resulting energy level alignments are summarized in correspondence with tandem OLED performance.

1. Introduction

Organic light-emitting diodes (OLEDs) are gaining the increasing importance in the applications of next-generation full-color display panels and solid-state lighting sources because they have a wide range of merits in mechanical flexibility, optical transparency, thin and light form factor, and superior color quality [1–3]. OLEDs with a tandem structure are considered to be of great promise for future general lighting systems, since multiple emission units are stacked electrically in series, featuring extremely high brightness at low current density with the dramatic boost in device stability and efficiency [3,4].

To realize highly efficient tandem OLEDs, the intermediate connectors functioning as charge generation layers (CGLs) play a pivotal role in facilitating the injection of electrons and holes into suitable molecular energy levels of adjacent emission units, which determine the electron-to-photon conversion process in tandem OLEDs [5–7]. Correspondingly, several criteria for the formation of an effective CGL are required, such as high charge-generation capability, low optical absorption in the visible spectral range, low series resistance for a minimal electrical loss, good operational stability and deposition compatibility [8–10].

Accordingly, an amount of approaches to design an efficient CGL have been proposed for realizing high-performance tandem OLEDs. The CGLs in tandem OLEDs typically consist of a bilayer structure with various materials, including a metal–metal (or metal oxide) bilayer [11], an organic–metal (or metal oxide) bilayer [5–9,12], or an organic–organic bilayer [4,7,13]. For the commonly used CGLs with an organic–metal oxide bilayer, transition metal oxides (TMOs) such as tungsten trioxide (WO_3) [11,12], molybdenum trioxide (MoO_3) [9,14], and vanadium oxide (V_2O_5) [15], are widely incorporated adjacent to the hole transport layer (HTL) of the neighboring emission unit. Meanwhile, the organic layers of a bilayer CGL are placed adjacent to the electron transport layer (ETL) of another neighboring emission unit, and commonly n-type doped by alkaline metals or metal compounds [4,6–12,16–18].

Regardless of the excellent device performance demonstrated in tandem OLEDs, the working mechanisms of charge generation and separation process in CGLs remain a subject of debate. Several models have been proposed for various CGL structures [13–22]. For the doped organic–organic bilayer CGL, a temperature-independent tunneling process was assumed for the charge generation, which was enabled by electric-field-induced electron transfer from the highest occupied molecular orbital (HOMO) of a p-type doped organic layer to the lowest unoccupied molecular orbital (LUMO)

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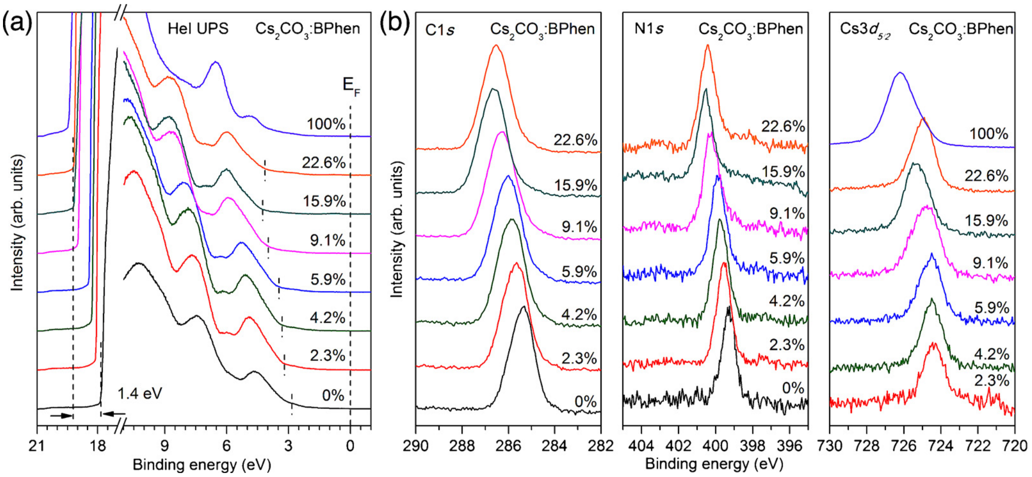

Fig. 1. Cs_2CO_3-induced n-type electrical doping. (a) UPS spectra of 10 nm-thick Cs_2CO_3-doped BPhen films as a function of Cs_2CO_3 doping concentration. (b) XPS spectra of C 1s, N 1s, and Cs $3d_{5/2}$ core levels of the corresponding Cs_2CO_3-doped BPhen films [25]. Copyright 2011, American Institute of Physics.

of an n-type doped organic layer [7,19]. However, different mechanisms have been put forward to unravel the charge carrier generation and separation process in TMO-based CGLs. One model suggested that charge generation and separation process was supposed to occur at the TMO/n-type doped organic interface by regarding TMOs as a p-type semiconductor [22]. On the contrary, another model for TMO-based CGLs attributed the thermally assisted charge generation at the TMO/HTL interface via electron transfer from the adjacent HTL's HOMO into the TMO's conduction band, since TMOs were demonstrated with n-type semiconducting character [21]. Consequently, the reliable information about interface energetics of the CGLs is highly desirable for understanding the working mechanisms of CGLs for interface engineering and the performance optimization of tandem OLEDs. Ultra-violet and X-ray photoemission spectroscopies (UPS and XPS) are the widely used techniques that provide the direct determination of energy level alignments (ELAs) at the organic interfaces.

In this review, we focus on our recent advances on TMOs-based CGLs in tandem OLEDs, especially from interface energetics perspective via photoemission spectroscopy. The electronic structures of various TMO-based CGLs and their role in charge generation process are reviewed. Here, the TMO-based CGLs consist of an n-type doped organic layer and a TMO layer, where WO_3 and MoO_3 are the most widely used TMOs in tandem OLEDs due to their favorable electronic properties, highly optical transparency in the visible region for photon output, and excellent fabrication compatibility. Section 2 discusses the n-type doping effect of organic layers with cesium compounds (i.e., CsF, CsN_3, and Cs_2CO_3). In Section 3, energetics at TMO/organic interfaces and the impact of annealing-induced oxygen vacancy on hole-injection barriers are overviewed as determined via photoemission spectroscopy. The ELAs and charge generation mechanisms of these TMO-based CGLs are addressed in Section 4. Finally, Section 5 provides a review of the influence of TMO-based CGLs on the performance characteristics of tandem OLEDs, particularly their stability on the device operational lifetime.

2. n-Type doping of organic layers with alkaline metal compounds

For commonly used CGLs consisting of a TMO-organic bilayer, the charge generation and separation process in tandem OLEDs was proposed to occur and operate effectively with the presence of an n-type doped organic layer [22,23]. Traditionally, electrical doping of organic layers is an efficient strategy to overcome their intrinsic limitations, e.g., low carrier transport conductivity and large charge injection barriers. For instance, *p–i–n* structures consisting of a p-type doped HTL, an intrinsic emission layer and an n-type doped ETL are generally considered as the state-of-the-art architecture for high-performance OLEDs due to the dramatically enhanced carrier transport properties with the highly reduced operating voltage [24]. Here, we address the n-type doping effect of organic materials with metal and metallic compounds in TMO-based CGLs and their influence on device performance of tandem OLEDs.

Compared to reactive metals as n-type dopants, the incorporation of alkaline metal compounds, e.g., cesium carbonate (Cs_2CO_3), cesium fluoride (CsF), cesium azide (CsN_3), etc., provides an effective approach for overcoming the limitations of low bulk conductivity and high electron injection barriers in organic layers due to the advantages for material handling and operational stability [4,6–12,16–18]. Despite the extensive utilization of alkaline metal compounds as n-type dopants in OLEDs to facilitate electron injection and reduce the Ohmic losses in organic layers, the nature of the incorporated species, the electronic structures of doped materials, and the working mechanisms of alkaline metal compounds as an n-type dopant in organic layers are not yet fully clarified. We have systematically studied the electronic structures and underlying physical mechanisms of n-type doped organic layers with various alkaline metal compounds via photoemission spectroscopy [17,25–27].

The doping effect of Cs_2CO_3 on electronic structures of 4,7-diphenyl-1,10-phenanthroline (BPhen), a typical organic ETL, was characterized with UPS and XPS measurements [25]. It can be observed from the UPS spectra in Fig. 1(a) that the increase of the Cs_2CO_3 doping concentration in BPhen films results in a gradual shift of the UPS spectral features toward higher binding energy (BE) region together with a vacuum level (VL) shift of 1.4 eV. Accordingly, it can be inferred that the Fermi level (E_F) in the Cs_2CO_3:BPhen layers moves within the energy gap toward the BPhen's LUMO, showing an n-type doping process. Fig. 1(b) displays the related evolution of XPS C 1s, N 1s, and Cs $3d_{5/2}$ core level spectra. Taking into account the original molecular ratios in pristine Cs_2CO_3, it is verified here that Cs_2CO_3 in n-type doped BPhen films is partially decomposed into cesium oxide during thermal evaporation, which is in agree with previous reports on thermal decomposition of Cs_2CO_3 [28]. The doping of Cs_2CO_3 into BPhen films imposes a progressive shift in general for C 1s and N 1s core levels toward higher BE region with respect to the increase in Cs_2CO_3 doping concentration, which is consistent with the behavior observed in the UPS spectra in Fig. 1(a). Compared to the case of pristine

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