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Interface electronic structures of organic light-emitting diodes with WO_3 interlayer: A study by photoelectron spectroscopy

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ABSTRACT

The energy level alignment and chemical reaction at the interface between the hole injection and transport layers in an organic light-emitting diode (OLED) structure has been studied using in-situ X-ray and ultraviolet photoelectron spectroscopy. The hole injection barrier measured by the positions of the highest occupied molecular orbital (HOMO) for *N,N′*-bis(1-naphthyl)-*N,N′*-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB)/indium tin oxide (ITO) was estimated 1.32 eV, while that with a thin WO_3 layer inserted between the NPB and ITO was significantly lowered to 0.46 eV. This barrier height reduction is followed by a large work function change which is likely due to the formation of new interface dipole. Upon annealing the WO_3 interlayer at 350 °C, the reduction of hole injection barrier height largely disappears. This is attributed to a chemical modification occurring in the WO_3 such as oxygen vacancy formation.

1. Introduction

OLEDs (organic light-emitting diodes) are display devices composed of multiple organic layers that create light by electron-hole recombination. The improvement of OLED performance has been achieved by controlling the charge carrier injection and transport passing through each layer. The inorganic/organic interfacial contact in OLEDs is important to charge injection and transport characteristics since the choice of interlayer structure has a large influence on the electron/hole injection efficiency. For instance, by adopting ultrathin metal oxides such as SiO_2, WO_3, MoO_3, and V_2O_5 layers between the anode and the hole transport layer (HTL), the OLED performance could be largely enhanced [1–5].

Among them, tungsten trioxide (WO_3) is lately drawing strong attention as a promising hole injection layer (HIL) since it has a very high work function (~6.2 eV) and is highly transparent in visible region [6]. The bulk structure of WO_3 has various phases at different temperatures. It is monoclinic at temperatures from 17 °C to 330 °C, orthorhombic from 330 °C to 740 °C, and tetragonal above 740 °C [7]. J. Meyer et al. reported that an OLED using the WO_3 layer exhibited a largely reduced operation voltage and its power efficiency was improved by about twice compared to the OLED without the WO_3 layer [6]. In addition, Li et al. reported that after thermal annealing WO_3 buffer layer at 450 °C, the structure of WO_3 was changed from amorphous to crystalline phase and consequently WO_3 further enhanced the device performance at the WO_3 thickness of 1.0 nm [8]. Also many other reports have shown that the WO_3 interlayer adopted as an HIL improved the device efficiency [9,10]. However, the mechanism for

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this improvement is not clearly understood yet at the film interface level. Therefore the elucidation of the interfacial electronic structures between anode and organic semiconductor is necessary for understanding and further improving the device performance.

In this paper, we will show ultraviolet photoelectron spectroscopy (UPS) studies of the *N,N′*-bis-(1-naphyl)-*N,N′*-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB)/indium tin oxide (ITO) interface, and the structure of a thin WO_3 layer inserted between the NPB and ITO anode. We have studied the change in the electronic structures and the energy level alignment at each interface. Also, to investigate the structural and chemical changes of WO_3 upon the annealing, X-ray photoelectron spectroscopy (XPS) is applied.

2. Experimental

The part of OLED structures used here were NPB/WO_3 on ITO substrate, in which the NPB, WO_3, and ITO covered glass substrate were used as HTL, HIL, and anode, respectively. ITO coated glass had been cleaned by chemicals and undergone a UV ozone treatment before insertion into a chamber. After each deposition of a target film, the sample was transferred to an analysis chamber without exposing to air. WO_3 layers were prepared below 2.0×10^{-7} Torr by thermal evaporation of WO_3 powder (99.99% purity) in a crucible wound with W filament for heating. NPB film was also deposited similar way. The film thickness was controlled by a quartz crystal microbalance. The typical deposition rate was 0.1 A/s. To investigate the influence of the WO_3 structural change on the interface, the WO_3 film was annealed in ultra high vacuum (UHV) at 350 °C for 15 min ($P = 2.0 \times 10^{-8}$ Torr) and subsequently cooled down to room temperature. The heating temperature was measured by a thermocouple connected to the sample.

The experiments were performed in an UHV system consisting of a sample preparation chamber and analysis chamber. The UPS spectra were recorded on VG ESCALAB 220i system with a hemispherical electron energy analyzer using a HeI (21.2 eV) gas discharge lamp. And the samples were biased to −10 and −5 V for the measurement of secondary cutoff region and near Fermi level (E_F, binding energy = 0), respectively. For XPS measurement, a Mg K_α (1253.6 eV) radiation was used as the excitation source. The XPS and UPS spectra were collected under normal emission.

A fitting procedure was performed on the W 4f spectra using an XPS curve fitting program. Each W 4f emission peak was fit with a doublet of Voigt functions with a constant branching ratio (0.75) and a spin-orbit splitting (2.12 eV) between $4f_{7/2}$ and $4f_{5/2}$.

3. Results and discussion

Fig. 1 shows the UPS spectra of secondary cutoff for work function measurement, valence band region, and the zooming in near E_F region, respectively as a function of NPB thickness on ITO film. Upon the adsorption of NPB, the film work function gradually decreases to 4.08 eV at the NPB thickness of 2 nm in Fig. 1a. The total work function change measures 0.74 eV possibly due to the formation of interface dipole between NPB and ITO [11,12]. The NPB/ITO interface spectra in Fig. 1b clearly show a series of characteristic peaks for the valence band structure of NPB at 9.1, 7.0, and 4.0 eV as the NPB thickness increases. Those peak positions are in good agreement with the previous results for the molecular orbitals of the NPB film [13–15]. In particular, the highest occupied molecular orbital (HOMO) is mainly localized on the N-nonbonding orbitals. As shown in the near E_F region of

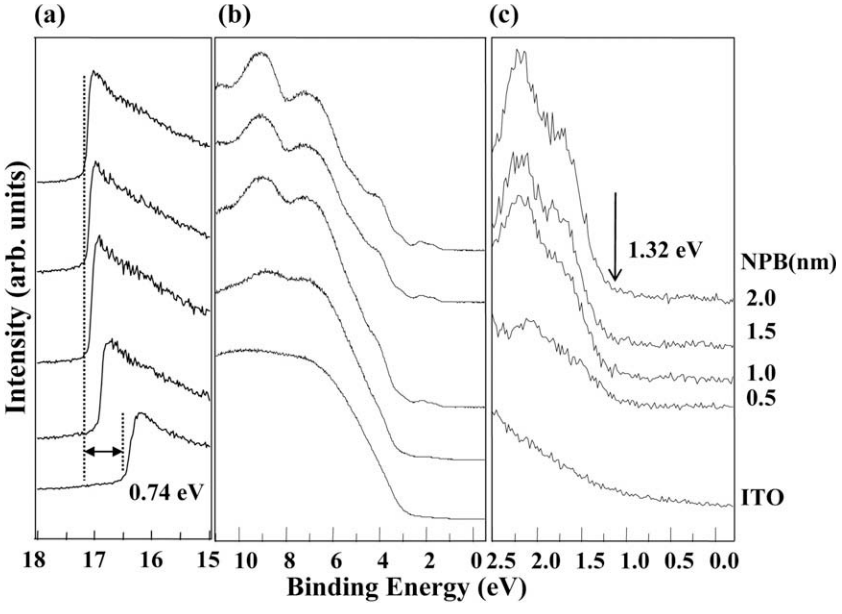

Fig. 1. UPS spectra as a function of NPB thickness on ITO substrates. (a) Secondary cutoff region, (b) valence band region and (c) near E_F region (arrow in graph: hole injection barrier height).