Interfacial electronic structure of molybdenum oxide on the fullerene layer, a potential hole-injecting layer in inverted top-emitting organic light-emitting diodes

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A R T I C L E   I N F O

Article history:
Received 10 July 2012
Received in revised form 9 January 2013
Accepted 13 February 2013
Available online 14 March 2013

Keywords:
Electronic structure
Inverted top-emitting organic light-emitting diode
Ultraviolet photoemission spectroscopy
X-ray photoemission spectroscopy
Near-edge X-ray absorption fine structure

A B S T R A C T

The interfacial electronic structures of molybdenum oxide (MoO₃) deposited on fullerene (C₆₀) which could be used as a hole-injecting layer in inverted top-emitting organic light-emitting diodes (TE-OLEDs) were investigated by photoemission spectroscopy. The hole-injecting barrier height (Φh) at each interface investigated by an ultraviolet photoemission spectroscopy was reduced to from 1.4 to 0.1 eV as the thickness of MoO₃ (θMoO₃) was increased from 0.1 to 5.0 nm on C₆₀. In these interface system, the sign of vacuum-level shift, highest occupied molecular orbital (HOMO)-level shift, and core-level shifts were all positive indicating that the interface mechanism is attributed to the work-function differences due to a band bending at these interfaces. Moreover, the near-edge X-ray absorption fine structure spectra at carbon K-edge did not show any structural modification as well as any chemical reaction at the MoO₃-on-C₆₀ interfaces when θMoO₃ was changed on C₆₀. From these results, the inverted TE-OLED with C₆₀ (5.0 nm)/MoO₃ (5.0 nm) showed the power efficiency of 1.7 lm/W at a luminance of about 1000 cd/m² and the maximum luminance of about 76,000 cd/m² at the bias voltage of 11.0 V. It exhibited the highest performance among the inverted TE-OLEDs fabricated as a function of MoO₃ thickness from 0 to 5.0 nm.

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1. Introduction

Organic light-emitting diode (OLED) display is not only one of the most promising next-generation flat panel displays but also an energy-efficient solid-state lighting source on account of their advantages such as self-emission, a simple structure, a high response speed, and a wide viewing angle [1–3]. For about a decade, active matrix (AM) OLED displays using thin film transistor backplane have been developed for pursuing higher resolution and lower power consumption [4]. It had been proved that the top-emission (TE) structure is suitable for high efficiency AM-OLED displays, since the structure allows the designing of a large aperture for high-resolution display, both without being bothered by the pixel circuits and with eliminating light-loss induced by waveguide effect in the glass substrate, which exist in conventional bottom-emission OLEDs [5]. Moreover, the inverted TE-OLED provides an advantage for making use of the n-channel a-Si thin film transistors, which could give more uniform brightness for a large area display.

Meanwhile, the interfaces between electrodes and organic layers are central to the physics of OLEDs, since the mismatch between the Fermi level (E_F) of electrodes and the organic (or inorganic) highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) controls the charge injection into the device. More specifically, low work function (Φ) cathodes and high Φ anodes are needed in order to fabricate efficient diodes by minimizing injection barriers [6]. The appropriate aligning of the relevant levels in organic (or inorganic)-electrode contact is necessary to maximize the luminous efficiency and minimize the power consumption by developing a low-voltage carrier-injecting layer. Also, a phenomenon occurring at an organic-electrode contact could be understood by interpreting various interface mechanisms, such as a chemical reaction, interface dipole by charge transfer, an image effect which is formed through either mirror force or surface rearrangement, a formation of either new interface states or permanent dipole, etc [6].

Recently, as p-type dopants, transition-metal oxides such as molybdenum oxides (MoO₃) [7–11] tungsten oxides (WO₃) [12], vanadium oxides (V₂O₃) [13], and ReO₃ [14] have been investigated as promising candidates to replace the organic hole injection layers, due to their stability and their high Φ. Among these p-type carrier-injecting layers, MoO₃ have been frequently used as

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http://dx.doi.org/10.1016/j.cap.2013.02.022
a hole-injecting layer (HIL) between a tin-doped indium oxide (ITO) layer and a hole-transporting layer (HTL) [7–11]. The MoOx-doped HILs and MoOx/HILs lead to an ohmic contact when inserted at between ITO and the HTL. Numerous studies have been reported to prove the reason why an ohmic contact is formed. It includes a formation of charge transfer complexes [9–11,15,16], a low hole-injecting barrier height (\(\Phi_h\)) and new metal-induced gap states below the \(E_F\) at these interfaces [7]. Since a contact between the electrode and the inorganic (or organic) is one of the most important factors in determining the device performance in OLEDs, it is imperative to understand and design the inorganic (or organic)-electrode interface.

In this paper, it was found that the MoOx-on-fullerene (C60) layers would be potential HILs in inverted TE-OLEDs [17]. The C60 layer consisting of HIL was introduced to increase the work function of Al anode. It has been reported that the work function of a metal can be increased by covering a thin layer C60 due to the strong redistribution of mobile charge carrier at metal/C60 interfaces [18,19], and efficient OLEDs were also fabricated using C60 as a HIL [20]. Therefore, in this study, MoOx-on-C60 was investigated as an HIL, even though MoOx itself has been widely used as a HIL for enhancing hole injection in OLEDs [21]. We report on an interface model as well as the \(\Phi_h\) at these interfaces, in which the electronic structure was investigated by various photoemission spectroscopic methods. Also, the correlation between the device performance of the inverted TE-OLED and the each interfacial electronic structure was discussed.

2. Experimental

The inverted TE-OLED has a p-Si/Aluminum (Al, 150 nm)/lithium fluoride (LiF, 1.0 nm)/tris(8-quinolinolato)aluminum (III) (Alq3, 40.0 nm)/N,N’-diphenyl-N,N’-bis(1-naphthyl)-1,4-biphenyl-4,4'-diamine (NPB, 60.0 nm)/C60 (5.0 nm)/MoOx (x nm)/Al (2.0 nm)/silver (Ag, 18.0 nm)/Alq3 (52.0 nm) structure. The bottom Al was used as a reflective cathode, LiF as an electron-injection layer (EIL), bottom Alq3 both as an electron-transporting layer (ETL) and a green emissive material layer (EML), NPB as a HTL, C60/MoOx as a HIL, Al/Ag as a semi-transparent anode [22], and top Alq3 as a capping layer, and they were sequentially vacuum-deposited by using a thermal evaporation system. The thickness of MoOx (\(\Theta_{MoOx}\)) on C60 in device I, device II, device III, and device IV was 0, 0.5, 1.0, and 5.0 nm, respectively. Also, the device V was consisted of 5 nm-thick MoOx only as a HIL. The emissive active area of the devices was 2 x 2 mm². The top capping layer of Alq3 (refractive index: 1.7) functions both as a transparent dielectric index-matching layer and as a semi-passivation layer [23]. The current density–voltage–luminance characteristics were measured using a Keithley 2400 electrometer, a photodiode (Oriel 71608), and a Keithley 485 picoammeter.

The electronic structures of the MoOx-on-C60 layers were investigated by using X-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the 4B1 beam line in the Pohang Accelerator Laboratory (Korea). All measurements and depositions were performed in an ultra-high vacuum system, consisting of a main analysis chamber (approximately 5 x 10^-10 Torr) and a sample preparation chamber (approximately 5 x 10^-8 Torr). For the analysis, all the samples were prepared in-situ via sequential thermal evaporation on a p-type Si wafer in an ultra-high vacuum system, which was connected to the beam line in vacuum. Also, all thicknesses were determined by timed depositions calibrated using a quartz-crystal microbalance. In the XPS studies, incident photon energies of 350 and 650 eV was used to obtain the core level spectra of carbon (C) 1s and oxygen (O) 1s, respectively. For the UPS measurements, the He I (21.2 eV) line from a UV source was used. The photoemission onset which reflects \(\Phi_h\) at the surface of all samples was measured by biasing the samples at -5 V. The incident photon energy was calibrated by measuring the Au 4f level of a clean Au surface. In the NEXAFS analyses, C K-edge (270–320 eV) spectra were measured at a photon incident angle of 45.0°.

3. Results and discussion

The metal oxide/organic interfaces (as a HIL) have been found to be critical in determining device performance of organic semiconductor such as OLEDs, organic transistors, and organic bulk hetero-junction solar cells. In an inverted TE-OLED structure, the metal oxide is placed on the organic layer, forming an organic/metal oxide interface [8]. To elucidate the mechanism involved in the light-emitting enhancement of the inverted TE-OLEDs, electronic structures of the MoOx-on-C60 interfaces were investigated by using various photoemission spectroscopic techniques as a function of \(\Theta_{MoOx}\). Especially, a robust interface is required with no potential barrier to carriers in order to prevent a Joule heating at the interface [24]. Also, the investigation of the energy levels of the MoOx-on-C60 interfaces is important in understanding the \(\Phi_h\) near the HIL/anode interface of the OLED structure investigated in this study. Fig. 1 shows the evolution of the He I valence band (VB) spectra of the pristine C60 and MoOx-on-C60 thin films with an incremental \(\Theta_{MoOx}\). The MoOx-on-C60 thin films were in-situ fabricated by sequentially depositing MoOx after pre-forming the 10.0 nm-thick C60 layer on a p-Si wafer. Fig. 1(a) and (b) exhibits the onset of VL representing \(\Phi\) on the surface and a HOMO region around the \(E_F\) of the MoOx-on-C60 layers, respectively. Also, the bar indicates the onset of the VL and HOMO in Fig. 1(a) and (b), respectively. As shown in the bottom curve of Fig. 1(a), the \(\Phi\) onset of the pristine C60 is positioned at 4.7 eV, which is equal to the photon energy (21.2 eV) minus VB width (16.5 eV) [6]. In the bottom curve of Fig. 1(b), the \(\Phi_{\text{HOMO}}\) which is the energy difference between the \(E_F\) of anode and the HOMO edge of pristine C60, is about 1.5 eV. The ionization energy of pristine C60, which is VL (4.7 eV) plus HOMO (1.5 eV), is measured as 6.2 eV in Fig. 1. In addition, the
pristine C$_{60}$ has a band gap of about 2.3 eV. It suffices to mention here that our data are in excellent agreement with previously published results [25].

In VB spectra of Fig. 1(b), the HOMO-1 (at around 3.5 eV) and HOMO (at around 2.1 eV) features present in pristine C$_{60}$ film [26]. Although the C$_{60}$ features attenuate with increasing a $\Theta_{MoO_x}$ on C$_{60}$, the molecular peaks remain clearly and all molecular levels steadily shift toward the $E_B$. When the $\Theta_{MoO_x}$ of 0.1 nm--5.0 nm was deposited on C$_{60}$, the $\Phi$ between Al anode and the MoO$_x$-on-C$_{60}$ interfaces were dramatically reduced from 1.3 to 0.1 eV. The decrease of $\Phi$ implies that a hole concentration could be largely increased in the MoO$_x$-on-C$_{60}$ interfaces. Also, in Fig. 1(a), the $\Phi$ at the MoO$_x$-on-C$_{60}$ interfaces showed the large rising up to 6.9 eV as the $\Theta_{MoO_x}$ was increased from 0.1 to 5.0 nm, when compared to that of pristine C$_{60}$ (4.7 eV).

Fig. 2(a) shows the XPS C 1s electron density curves (EDCs) measured as a function of a $\Theta_{MoO_x}$ on 10 nm-thick C$_{60}$. For the pristine C$_{60}$, the C core-level EDC was symmetrical in shape and was composed of a single component, indicating a clean C$_{60}$ film. For the pristine C$_{60}$, the peak is located at the binding energy ($E_B$) of 284.7 eV and is well coincide with the published data of pristine C$_{60}$ [25]. For $\Theta_{MoO_x} = 0.1$ nm, the C 1s EDC was shifted to a little lower $E_B$ of 284.6 eV and was shifted further to 283.4 eV as the $\Theta_{MoO_x}$ is increased to 5.0 nm. This peak shift to a lower $E_B$ was caused by a decrease in the Coulomb potential between the nuclei and the electron of the valence band as a result of the increased electron density at the valence band of carbon atoms due to $\Phi$ difference.

The $E_B$ rising of 1.3 eV with the increase of $\Theta_{MoO_x}$ from 0 to 5 nm showed the similar trend to the shifts of both the HOMO and $\Phi$ levels in Fig. 1. Fig. 2(b) shows XPS O 1s core level EDCs as a function of the $\Theta_{MoO_x}$ on 10.0 nm-thick component. At the $\Theta_{MoO_x} = 0.1$ nm, the symmetrical O 1s peak appears at 532.6 eV. As the $\Theta_{MoO_x}$ was increased from 0.1 to 5.0 nm on C$_{60}$, the $E_B$ was largely shifted by 2.2 eV toward lower binding energy. Because the signs of the energy shifts are all positive for the EDCs of C and O, it is believed that the $E_B$ shift to a lower energy observed in Fig. 2 is originated from the band bending not from electron charge transfer between C$_{60}$ and MoO$_x$. This result implies that interface dipole by electron charge transfer is not occurred at these interfaces.

To identify whether additional chemical reactions and/or electron charge transfers occur or not between the MoO$_x$ and C$_{60}$ interfaces, the NEXAFS spectra were investigated. The NEXAFS spectroscopy shows the resonance features induced by the absorption of X-rays that excite electrons from the initial state (core level) to the final state (vacant level) and can be used to obtain information on both the core levels and the unoccupied states. Fig. 3 shows the total electron yield (TEY) NEXAFS spectra, which are measured at the photon incident angle of 45.0°, for the K-edge of the pristine C$_{60}$ and the MoO$_x$-on-C$_{60}$ interfaces with increasing the $\Theta_{MoO_x}$ on C$_{60}$ of 10 nm. The C K-edge 1s $\rightarrow$ $\pi^*$ resonances of pristine C$_{60}$ in Fig. 3 were 284.5 (LUMO), 286.3 (LUMO+1 and LUMO+2), and 288.5 eV (LUMO+3), respectively, with allowing a straightforward peak assignment [27]. This alignment means a transition involved to the conjugation of C$_{60}$. When MoO$_x$ of 0.1--5.0 nm is deposited on C$_{60}$, the main features of the 1s $\rightarrow$ $\pi^*$ energy shift remain clearly unchanged and the intensity change of the $\pi^*$-derived exciton peaks is negligible, as deduced by the direct comparison of the spectra for different coverage. This indicates that any structural modification as well as any chemical reaction is not occurred at the MoO$_x$-on-C$_{60}$ interface because the core level and vacant levels are not changed at TEY-NEXAFS spectra. Fig. 4 exhibits the onsets of the energy levels ($\Phi$, HOMO, LUMO, and $E_0$) in the MoO$_x$-on-C$_{60}$ interfaces, obtained from the results in Figs. 1 and 2. In this interface system, the sign of $\Phi$ shift, HOMO-level shift, and core-level shifts are all positive. The large rising of all energy levels are attributed to the work-function differences due to band bending, not being occurred from interfacial dipole effect due to electron charge transfer between MoO$_x$ and C$_{60}$.

Fig. 5 shows the proposed energy band diagram for the hole injection at both the Al/MoO$_x$/C$_{60}$ and C$_{60}$/NPB interfaces. Fig. 5(a) exhibits the $\Phi$ of 1.5 eV between Al anode and pristine C$_{60}$. As $\Theta_{MoO_x}$ is increased from 0.4 to 5.0 nm on C$_{60}$, it is shown that the $\Phi^*$ can reduce from 1.1 to 0.1 eV. The low $\Phi$ at high $\Theta_{MoO_x}$ explains that a hole is efficiently injected from the Al anode to the MoO$_x$/C$_{60}$ layer. Also, as shown in Fig. 5(b), the $\Phi$ from C$_{60}$ to NPB does not

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**Figure 2.** (a) C 1s and (b) O 1s XPS core-level EDCs measured as a function of $\Theta_{MoO_x}$ on the 10.0 nm-thick C$_{60}$ layer. The values in the figures indicate the thickness of $\Theta_{MoO_x}$.

**Figure 3.** TEY-NEXAFS spectra at the C K-edge of the MoO$_x$-on-C$_{60}$ interfaces. The values in the figures indicate the thickness of $\Theta_{MoO_x}$ on the 10.0 nm-thick C$_{60}$ layer.
exist in the energy band diagram because the HOMO level of C60 is higher than that of NPB, thereby expecting an improvement in the hole-injecting property at the Al/MoOx/C60/NPB interfaces. Moreover, this result proves that the MoOx-on-C60 layers can serve as a potential material to improve a p-type contact in inverted TE-OLEDs.

Up to now, the electronic structures of the MoOx-on-C60 interfaces were investigated to apply their interfacial characteristics to inverted TE-OLEDs. The inverted TE-OLEDs composed of a p-Si/Al (150 nm)/LiF (1.0 nm)/Alq3 (40.0 nm)/NPB (60.0 nm)/C60 (5.0 nm)/MoOx (x nm)/Al (2.0 nm)/Ag (18.0 nm)/Alq3 (52.0 nm) structure which includes the MoOx-on-C60 interfaces were fabricated to study the effect of MoOx in these MoOx-on-C60 interfaces by measuring the electrical characteristic of the OLEDs. Fig. 6(a) shows the current density–voltage characteristics of the inverted TE-OLEDs, which were obtained to optimize the θMoOx on the MoOx-on-C60 layer. The

![Image](image-url)

**Fig. 4.** Energy levels of the MoOx-on-C60 interfaces as a function of θMoOx on the 10.0 nm-thick C60 layer.

![Image](image-url)

**Fig. 5.** Proposed energy band diagrams at both the Al/MoOx/C60 (a) and C60/NPB interfaces (b).

![Image](image-url)

**Fig. 6.** (a) Current density–voltage characteristics of the inverted TE-OLEDs with various θMoOx. The device structure is composed of p-Si/Al (150 nm)/LiF (1.0 nm)/Alq3 (40.0 nm)/NPB (60.0 nm)/C60 (5.0 nm)/MoOx (x nm)/Al (2.0 nm)/Ag (18.0 nm)/Alq3 (52.0 nm). Here, x is 0 (device I), 0.5 (device II), 1.0 (device III), and 5.0 nm (device IV), respectively. The device V has only the sole MoOx layer of 5 nm-thick instead of the C60/MoOx layer as a HIL. The inset of Fig. 6(a) shows the luminance as a function of bias voltage in each device. (b) Power efficiency–current density (closed dots) and external quantum efficiency–current density characteristics (open dots) for the devices I, II, III, and IV.
\( \Theta_{\text{MoO}_x} \) of the devices I, II, III, and IV were 0, 0.5, 1.0, and 5.0 nm, respectively. As shown in the figure, the device IV with \( \Theta_{\text{MoO}_x} \) of 5.0 nm on C60 as HTLs exhibited the lowest operating voltage of 7.8 V at the current density of about 20 mA/cm². In contrast, the devices with the \( \Theta_{\text{MoO}_x} \) of less than 5.0 nm on C60 showed higher operating voltages of 16.2, 11.0, and 9.4 eV for the devices I, II, and III, respectively, at a constant current density of about 20 mA/cm². Also, the device V, which has MoO only as a HIL, exhibited 8.2 V of operating voltage which is higher than that of the device IV as shown in Fig. 6(a). It is believed that C60 in the C60/MoO₂ bilayer structure as the HIL plays an important role in improving the overall injection process through the low \( \Phi_b \), due to the positive enhanced band bending as explained in Figs. 4 and 5, compared to MoO only as the HIL. Meanwhile, the turn-on voltage (\( V_t \)) at a luminance of about 0.01 cd/m² for the devices I, II, III, and VI were 5.8, 4.2, 3.0, and 2.8 V, respectively. Clearly, at a given luminance, the device IV showed a lower driving voltage than the other three devices.

The deriving voltage is significantly decreased as a \( \Theta_{\text{MoO}_x} \) is increased, indicating that the interface resistance of the MoO₂-on-C60 layer is reduced. In the case of the maximum luminance (\( L_{\text{max}} \)), the device IV as shown in the inset of Fig. 6(a) showed the highest \( L_{\text{max}} \) of 76000 cd/m² at the voltage of 11.0 V among the devices investigated.

Fig. 6(b) shows both the power efficiency (\( \eta_{\text{PE}} \): closed dots) and external quantum efficiency (\( \eta_{\text{EQE}} \): open dots) measured as a function of the current density of each device. The \( \eta_{\text{PE}} \) values at the luminance of 1000 cd/m² (\( L_{1000} \)) were 0.2 (17.2), 0.8 (10.0), 1.2 (8.8), and 1.7 lm/W (7.6 V), for the devices I, II, III, and IV, respectively. Also, The \( \eta_{\text{EQE}} \) values at the luminance of 1000 cd/m² (\( L_{1000} \)) were 0.1 (17.2), 0.6 (10.0), 0.9 (8.8), and 1.2% (7.6 V), for the devices I, II, III, and IV, respectively. The device characteristics such as \( \Phi_b \), \( L_{\text{max}} \), \( \eta_{\text{PE}} \), and \( \eta_{\text{EQE}} \) were compared among the devices in Fig. 6(b), the device IV with the MoO₂-(5.0 nm)-on-C60-(5.0 nm) also showed the best light-emitting properties. The current density—voltage—luminance characteristics were in well agreement with the reduction of the \( \Phi_b \) in the MoO₂-on-C60 layers due to the positive band bending as already shown in Figs. 1 and 2, functioning as a better hole conductor with increasing the \( \Theta_{\text{MoO}_x} \) on C60.

4. Conclusions

The interface mechanism of MoO₂-on-C60 was originated from the \( \Phi \) difference due to the band bending, not being occurred from interfacial dipole effect by electron charge transfer. Moreover, TEY-NEXAFS spectra at the C K-edge did not show any structural modification as well as any chemical reaction. In the energy level studies by UPS and XPS, the sign of an \( \Phi \) shift, HOMO-level shift and core-level shifts (C 1s and O 1s) were all positive. Therefore, \( \Phi_b \) was reduced to 0.1 eV by simple band bending, with increasing the \( \Theta_{\text{MoO}_x} \) to 5 nm on the MoO₂-on-C60 interfaces. The characteristics of these electronic structures are in well agreement to the device performance of inverted TE-OLEDs with these interfaces. The optimized device exhibited both the \( \eta_{\text{PE}} \) of 1.7 lm/W at the luminance of 1000 cd/m² and the \( L_{\text{max}} \) of 76000 cd/m² at the bias voltage of 11.0 V.

Acknowledgments

This work was supported in part by the World Class University program of National Research Foundation of Korea (Grant No. R32-10124) and was supported by the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2010-M1A2A01-2010-0026248) and was supported by Pohang Accelerator Laboratory in Korea.

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