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Description	



Formation of Ohmic hole injection by inserting an ultrathin layer of molybdenum trioxide between indium tin oxide and organic hole-transporting layers

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Current density–voltage (J - V) characteristics of hole-only devices using indium tin oxide (ITO) anode and N,N' -diphenyl- N,N' -bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD) layers were measured with various thicknesses of a molybdenum trioxide (MoO_3) buffer layer inserted between ITO and α -NPD. The device with a 0.75-nm-thick MoO_3 layer forms Ohmic hole injection at the ITO/ MoO_3 / α -NPD interfaces and J - V characteristics of this device are controlled by a space-charge-limited current. Results of X-ray photoelectron and ultraviolet/visible/near-infrared absorption studies revealed that this Ohmic hole injection is attributable to an electron transfer from ITO and α -NPD to MoO_3 . © 2007 American Institute of Physics. [DOI: 10.1063/1.2825275]

Organic light-emitting diodes (OLEDs) are being developed due to their high potentials for use in low-cost, mechanically flexible, and lightweight display, and lighting applications.¹ Multilayer OLEDs are typically composed of an indium tin oxide (ITO) anode, an organic hole-transporting layer (HTL), an emitting layer, an electron-transporting layer, and a metal cathode.² N,N' -diphenyl- N,N' -bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD) is a material that is widely used as a HTL in OLEDs.^{3–6} In OLEDs with the ITO anode and the α -NPD HTL, a hole injection barrier of ≈ 0.4 eV at the ITO/ α -NPD interface is present⁷ and causes an increase in driving voltage. Various organic and inorganic hole-injecting layers (HILs) have been inserted between ITO and α -NPD to reduce the driving voltages.^{3,8–13} Recently, Chu and Song reported that a quasi-Ohmic contact was realized by inserting a 2.5-nm-thick C60 layer between ITO and α -NPD, which reduces the hole injection barrier by the surface dipole formation.^{12,13} They observed Schottky thermoionic currents at low voltages and space-charge-limited currents (SCLCs) at high voltages. The SCLC slope of 2.4 was slightly higher than that of the prediction of the SCLC theory. Thus, Ohmic contacts have never been achieved at the ITO/HIL/ α -NPD interfaces to date. If Ohmic contacts can be formed, further improvements of driving voltages and power conversion efficiencies of OLEDs are possible.

Besides the improvements in OLED performance, understanding carrier transport mechanisms in organic films is very crucial as fundamental science.^{14–16} However, the carrier transport mechanisms have not yet been elucidated, and must be further clarified to bring about maximum device performance. Large carrier injection barriers at electrode/HTL interfaces would make the carrier transport mechanisms complex because observed currents are governed by both carrier injection and transport.¹⁵ Therefore, the formation of Ohmic contacts at the interfaces is indispensable to clarifying the carrier transport mechanisms.

In this study, we found that insertion of an ultrathin molybdenum trioxide (MoO_3) HIL between ITO and α -NPD

provides Ohmic hole injection at the interfaces. We fabricated hole-only α -NPD devices with a glass substrate/ITO anode (150 nm)/ MoO_3 HIL (X nm)/ α -NPD HTL (L nm)/ MoO_3 electron-blocking layer (EBL) (10 nm)/Al cathode (100 nm) structure. We investigated how the X 's and L 's influence current density–voltage (J - V) characteristics of the devices. MoO_3 has already been used as a HIL to reduce driving voltages of OLEDs.^{9–11} Although the thickness of MoO_3 HILs previously used is in the range between 5 and 50 nm, the results in the present study clearly indicated that such thick MoO_3 HILs do not provide Ohmic hole injection. We found that the optimized X is 0.75 nm, which is much thinner than the previously reported values. The α -NPD device with a 0.75-nm-thick MoO_3 HIL exhibited $J \propto V^{2.0}$ characteristics, indicating that this device achieves Ohmic hole injection and that J - V characteristics of this device obey a SCLC mechanism.

We fabricated the α -NPD devices according to the following procedure. Precleaned glass substrates coated with a 150-nm-thick ITO layer with a sheet resistance of 10 Ω /sq (SLR grade, Sanyo Vacuum Industries Co., Ltd.) were set in a vacuum evaporator, which was evacuated to $\approx 10^{-4}$ Pa. A MoO_3 HIL (X nm), an α -NPD HTL (L nm), and a MoO_3 EBL (10 nm) were successively vacuum deposited on the ITO surface at deposition rates of 0.05 nm/s for MoO_3 and 0.1 nm/s for α -NPD. We varied the thickness of the MoO_3 HIL (X) from 0 to 20 nm and varied the thickness of the α -NPD HTL (L) from 50 to 300 nm. To complete the devices, an Al cathode layer (100 nm) was vacuum deposited on the MoO_3 EBL at a deposition rate of 0.3 nm/s through a shadow mask to define the active area of the devices to be 4 mm². High-purity MoO_3 (6N grade, Mitsuwa Chemicals Co., Ltd), α -NPD (NN60615, Nippon Steel Chemical Co., Ltd.), and Al (AL-011480, Nilaco Co.) source materials were purchased and used as received. The completed devices were transferred to a nitrogen-filled glovebox (O_2 and H_2O levels less than 2 ppm) and encapsulated with a glass cap and an ultraviolet curing epoxy resin. J - V characteristics of the devices were measured using a semiconductor characterization system (SCS4200, Keithley Instruments, Inc.) at room temperature.

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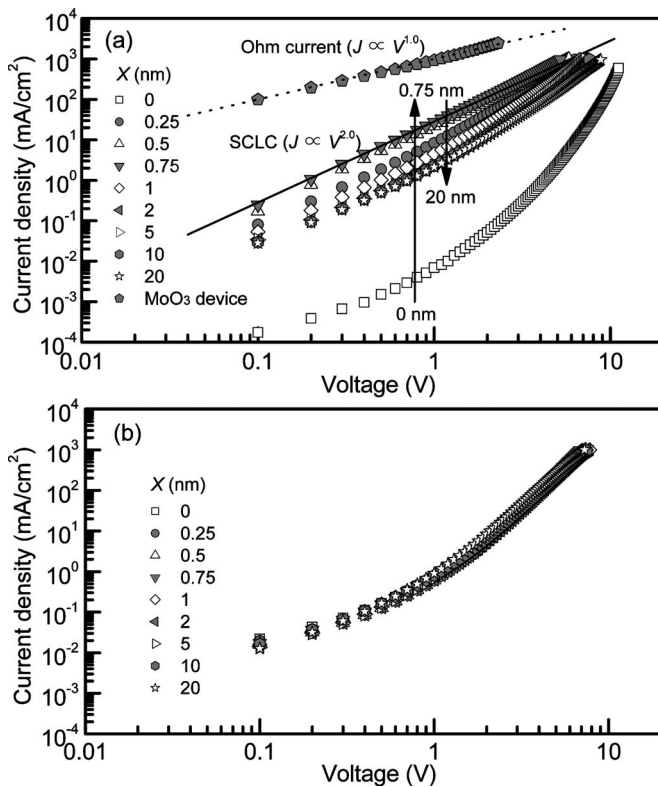


FIG. 1. Current density–voltage characteristics of hole-only α -NPD devices with various X 's and L of 100 nm at (a) forward bias and (b) reverse bias. The solid and dotted lines represent SCLC and Ohm current, respectively.

In our devices, we inserted the high-work-function MoO_3 EBL (-5.68 ± 0.03 eV⁷) at the α -NPD/Al interface to prevent electron injection from Al. In fact, since we observed no electroluminescence from the devices, we confirmed that holes are dominant charge carriers. The J - V characteristics of the devices with various X 's and a constant L of 100 nm are shown in Fig. 1(a).

The J 's markedly increased when increasing the X 's from 0 to 0.75 nm. The device with a X of 0.75 nm exhibited the highest J and a square law ($J \propto V^{2.0}$). Reversely, the J 's decreased when increasing the X 's from 0.75 to 2 nm. The J - V characteristics became unchanged in the X range between 2 and 20 nm. From these results, we conclude that the device with an X of 0.75 nm can achieve Ohmic hole injection and that the J - V characteristics of this device are controlled by a SCLC. We confirmed that an electron transfer from ITO and α -NPD to MoO_3 occurs. The evidence of the charge transfer is presented later. The charge transfer must induce matching among the Fermi levels of MoO_3 and ITO and the hole transport level of α -NPD, resulting in the formation of the Ohmic contact. On the other hand, we speculate that a strong interfacial dipole layer (IDL), i.e., negatively charged MoO_3 and positively charged α -NPD, is gradually formed at the MoO_3/α -NPD interfaces as increasing the X 's from 1 to 20 nm. This IDL may lower carrier injection at the interfaces.¹⁷

We prepared a device with a glass substrate/ITO anode (150 nm)/ MoO_3 layer (100 nm)/Al cathode (100 nm) structure. The J 's observed in the MoO_3 device were much higher than those observed in the α -NPD devices [Fig. 1(a)]. Moreover, this device exhibited an Ohmic current. The electrical conductivity of the MoO_3 layer was calculated to be $1.0 \pm 0.1 \times 10^{-5}$ S/cm from the $J \propto V^{1.0}$ region [the dotted

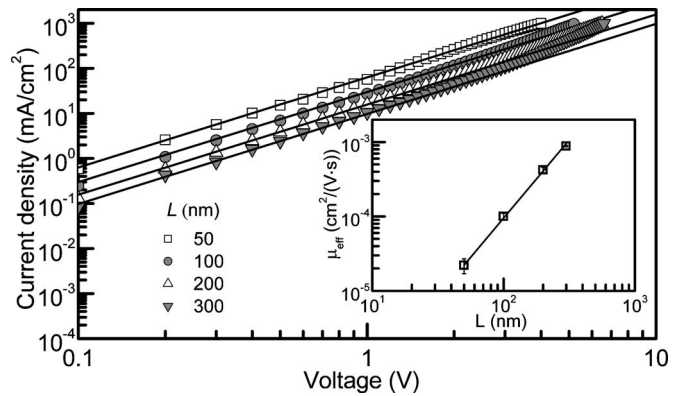


FIG. 2. Current density–voltage characteristics of forward biased hole-only α -NPD devices with constant X of 0.75 nm and various L 's. The solid lines represent calculated J - V curves based on SCLC theory. The inset shows effective hole-mobility-thickness characteristics.

line shown in Fig. 1(a)], which is in the semiconductorlike range and is about seven orders of magnitude lower than that of a radio-frequency magnetron-sputtered MoO_3 layer (≈ 80 S/cm) having a nearly stoichiometric composition.⁹ This low electrical conductivity is perhaps caused by the difference in composition and grain size between the vacuum-deposited and sputtered films.

We operated the α -NPD devices with various X 's and a L of 100 nm in the reverse bias direction. While the J - V characteristics of the forward biased devices were markedly dependent upon X [Fig. 1(a)], the J - V characteristics of the reverse biased devices were independent of X [Fig. 1(b)]. We attribute the unchanged J - V characteristics to (1) insertion of the MoO_3 layer with a constant thickness of 10 nm between α -NPD and Al and (2) the use of the MoO_3 layers, which may work as electrodes in the devices.

We found that the J - V characteristics of the devices with an X of 0.75 nm are well described by a SCLC mechanism,¹⁴ whose equation is given by, $J = (9/8) \epsilon_r \epsilon_0 \mu_{\text{eff}} (V^2/L^3)$ (1), where ϵ_r is relative permittivity, ϵ_0 is vacuum permittivity, and μ_{eff} is effective carrier mobility. Fitting the J - V characteristics using Eq. (1) with a ϵ_r of 3.0 (Ref. 12) provides a μ_{eff} of $(1.0 \pm 0.1) \times 10^{-4}$ cm²/V s [the solid line shown in Fig. 1(a)].

We investigated how the L 's influence hole transport in the devices with a constant X of 0.75 nm. The J 's decreased as the L 's were increased and all devices had a square law (Fig. 2). The μ_{eff} 's were calculated to be $(2.2 \pm 0.5) \times 10^{-5}$ cm²/V s for $L=50$ nm, $(4.2 \pm 0.4) \times 10^{-4}$ cm²/V s for $L=200$ nm, and $(8.8 \pm 0.2) \times 10^{-4}$ cm²/V s for $L=300$ nm from the $J \propto V^{2.0}$ regions (the solid lines in Fig. 2). The observed μ_{eff} 's markedly depended on the L 's (the inset in Fig. 2).¹⁸ Although the μ_{eff} for $L=50$ nm was much smaller than those of thick α -NPD layers measured by a time-of-flight (TOF) technique [$(3.0\text{--}10.0) \times 10^{-4}$ cm²/V s (Ref. 4 and 5)], the μ_{eff} for $L=300$ nm was in excellent agreement with the TOF mobilities. Similar thickness-dependent mobilities were recently reported by Chu and Song.¹² They attributed the thickness-dependent mobilities to the change of hole trap concentrations in the α -NPD films.

Recently, a SCLC with electric-field-, temperature-, and charge-carrier-concentration-dependent carrier mobilities for disordered hopping transport in organic films has been modeled by Pasveer *et al.*¹⁶ We suppose that the difference be-

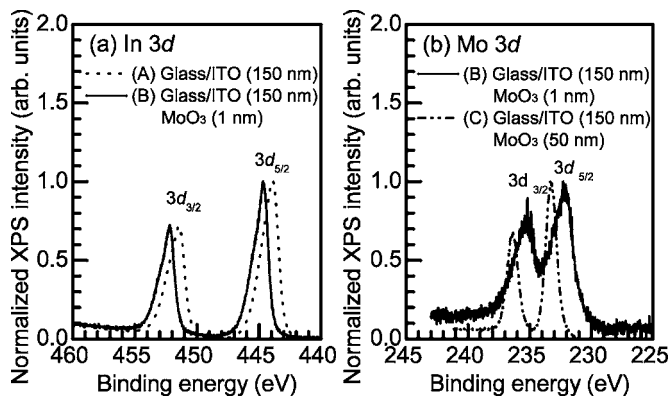


FIG. 3. XPS spectra: (a) In $3d$ peaks observed in (A) glass substrate/ITO layer (150 nm) and (B) glass substrate/ITO layer (150 nm)/MoO₃ layer (1 nm), and (b) Mo $3d$ peaks observed in (B) and (C) glass substrate/ITO layer (150 nm)/MoO₃ layer (50 nm).

tween the experimental data and Eq. (1) at high current densities (Fig. 2) is caused by Pasveer's mobility effect.

To investigate the origin of the formation of the Ohmic hole injection, we measured x-ray photoelectron spectra (XPS) using an ESCA5600 spectrometer. We prepared three samples for XPS: (A) glass substrate/ITO layer (150 nm), (B) glass substrate/ITO layer (150 nm)/MoO₃ layer (1 nm), and (C) glass substrate/ITO layer (150 nm)/MoO₃ layer (50 nm). We only observed XPS peaks originating from ITO in (A) and XPS peaks originating from MoO₃ in (C). On the other hand, there were XPS peaks originating from both ITO and MoO₃ in a XPS spectrum of (B) due to the preparation of an ultrathin MoO₃ layer on ITO. The In $3d$ peaks shifted to higher energies [Fig. 3(a)] and the Mo $3d$ peaks shifted to lower energies [Fig. 3(b)] in the XPS spectra of (B) when compared with those in the XPS spectra of (A) and (C). Since a negatively charged atom has a higher binding energy of electrons, these spectral shifts mean an electron transfer from ITO to MoO₃.

We prepared 50-nm-thick films of α -NPD, MoO₃, and a composite of α -NPD and MoO₃ (1:1 by mole) on quartz substrates, and measured their ultraviolet/visible/near-infrared (UV-vis-NIR) absorption spectra using a V-570 spectrometer (JASCO Co.). Compared with the absorption spectra of the α -NPD and MoO₃ films, a broad absorption peak appeared at around 1350 nm in the absorption spectra of the composite film (Fig. 4). A similar result was reported by Ikeda *et al.*¹⁹ The observation of this peak is proof of an electron transfer from low-ionization-potential-energy α -NPD (-5.02 ± 0.02 eV⁷) to high-work-function MoO₃ (-5.68 ± 0.03 eV⁷). From the results of the XPS and UV-vis-NIR absorption studies, we conclude that an electron transfer from ITO and α -NPD to MoO₃ occurs and induces the shifts among the Fermi levels of MoO₃ and ITO and the hole transport level of α -NPD, leading to the Ohmic hole injection at the ITO/MoO₃/ α -NPD interfaces.

In summary, we investigated J - V characteristics of hole-only α -NPD devices with a MoO₃ HIL with various thicknesses. Results of extensive J - V , XPS, and UV-vis-NIR absorption studies demonstrated that (1) the device with a 0.75-nm-thick MoO₃ HIL can achieve Ohmic hole injection, (2) J - V characteristics of the device with a 0.75-nm-thick

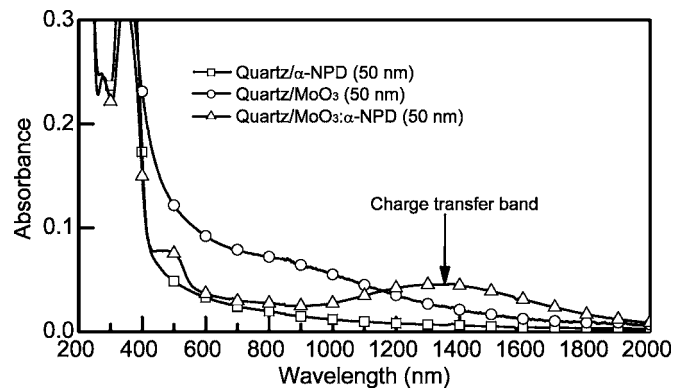


FIG. 4. UV-vis-NIR absorption spectra of α -NPD layer (50 nm), MoO₃ layer (50 nm), and 50 mol % MoO₃-doped α -NPD layer (50 nm) prepared on quartz substrates.

MoO₃ HIL are controlled by a SCLC with thickness-dependent hole mobilities, and (3) the formation of the Ohmic hole injection is attributable to an electron transfer from ITO and α -NPD to MoO₃. Finally, we emphasize that this Ohmic hole injection effect by using the ultrathin MoO₃ HIL is not only valuable in reducing driving voltages of organic electronic devices but also clarifying the underlying mechanisms of carrier transport in organic films.

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