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## Observation of space-charge-limited current due to charge generation at interface of molybdenum dioxide and organic layer

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Current density-voltage characteristics of hole-only devices are influenced by thicknesses of molybdenum dioxide ( $\text{MoO}_2$ ) and molybdenum trioxide ( $\text{MoO}_3$ ) as buffer layers. A space-charge-limited current of  $N,N'$ -diphenyl- $N,N'$ -bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine ( $\alpha$ -NPD) is observed in a wide range of  $\text{MoO}_2$  thicknesses from 0.25 to 10 nm and at a specific  $\text{MoO}_3$  thickness of 0.75 nm. Charge transfer characteristics at interfaces of  $\text{MoO}_2/\alpha$ -NPD and  $\text{MoO}_3/\alpha$ -NPD are investigated from changes in fluorescence intensity of  $\alpha$ -NPD. Reasons of the improved device characteristics are discussed in terms of interfacial charge generation composed of charged transfer and charge separation. © 2009 American Institute of Physics. [doi:10.1063/1.3267082]

A multilayer structure has been adopted in organic light-emitting diodes (OLEDs) to improve luminous efficiencies.<sup>1</sup> Due to the multilayer structure, there are multiple energy barriers for charge injection at interfaces of electrode/organic and organic/organic heterojunctions. The barriers frequently degrade OLED performance<sup>2,3</sup> and make analyzing a charge transport mechanism of organic films difficult because observed currents are governed by both charge injection and transport. Therefore, designing barrier-free device structures is crucial to understanding the mechanism as well as improving the performance.

Recently, it has been shown that inserting molybdenum trioxide ( $\text{MoO}_3$ ) as a buffer layer (0.75 nm) between indium tin oxide (ITO) and  $N,N'$ -diphenyl- $N,N'$ -bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine ( $\alpha$ -NPD) leads to an increase in current by  $\approx 10^4$  and observation of a space-charge-limited current (SCLC),<sup>4</sup> indicating that the barrier is negligible. Also, power consumption and lifetimes of OLEDs have been improved by using  $\text{MoO}_3$ .<sup>3</sup> Although changes in electronic states (Fermi level shifts and band bending) have been observed in multilayer films of ITO/ $\text{MoO}_3/\alpha$ -NPD and  $\text{MoO}_3$ -doped films using ultraviolet photoelectron spectroscopy,<sup>5,6</sup> the origins of the improved device characteristics have not been clarified. In this study, we show that molybdenum dioxide ( $\text{MoO}_2$ ) acts as an excellent buffer layer as well. The SCLC is observed in a wide range of  $\text{MoO}_2$  thicknesses from 0.25 to 10 nm in contrast to the specific  $\text{MoO}_3$  thickness. Although we previously attributed the SCLC observed to Ohmic injection,<sup>4</sup> in this letter, we propose a charge generation mechanism to explain why the SCLC is observed.

The hole-only devices were fabricated as previously reported (Refs. 3 and 4). The device structures were glass substrate/ITO (150 nm)/ $\text{MoO}_2$  ( $X$  nm) or  $\text{MoO}_3$  ( $Y$  nm)/ $\alpha$ -NPD (100 nm)/ $\text{MoO}_2$  or  $\text{MoO}_3$  (10 nm)/Al (100 nm), where  $X$  and  $Y$  are changed from 0 to 10 nm. The current density-voltage ( $J$ - $V$ ) characteristics of the devices were measured using a SCS4200 semiconductor character-

ization system (Keithley) at room temperature.

The  $J$ - $V$  characteristics of the devices are shown in Figs. 1(a) and 1(b), respectively. The  $J$  at an  $X$  and a  $Y$  of 0 nm is present in a lower current region. The  $J$  increases  $\approx 10^4$  times by using the  $\text{MoO}_2$  ( $\text{MoO}_3$ ). While the  $J$  is independent of the  $X$ , the  $J$  is dependent upon the  $Y$ . After the  $J$  reaches the highest level at a  $Y$  of 0.75 nm, the  $J$  decreases by  $\approx 10^1$  at higher  $Y$ .<sup>4</sup>

If a free charge density is negligible in comparison to an injected charge density, the equation of a SCLC with field-dependent mobilities<sup>7</sup> is given by

$$J = (9/8)\epsilon_r\epsilon_0\mu_0 \exp[0.89\beta(V/L)^{0.5}](V^2/L^3), \quad (1)$$

where  $\epsilon_r$  is relative permittivity,  $\epsilon_0$  is vacuum permittivity,  $\mu_0$  is zero field mobility,  $\beta$  is field dependence parameter,

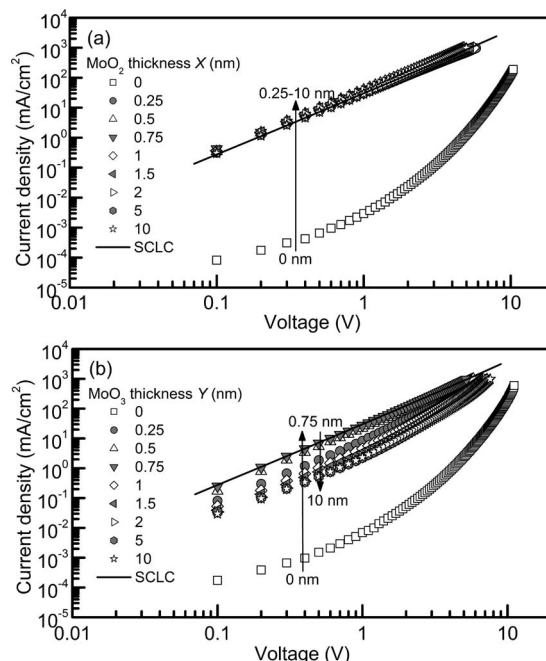


FIG. 1.  $J$ - $V$  characteristics of devices, where (a)  $X$  and (b)  $Y$  are changed from 0 to 10 nm. Solid lines represent SCLC.

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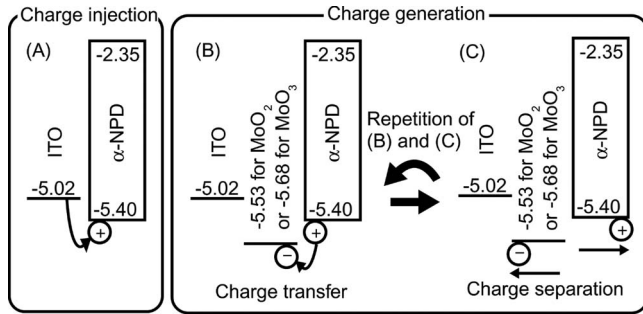


FIG. 2. Illustrations of energy-level diagrams to explain charge injection (A) and charge generation composed of charge transfer (B) and charge separation (C). Diagrams are estimated as previously reported (Refs. 3 and 4).

and  $L$  is thickness. The equation is valid because an  $\alpha$ -NPD thickness (100 nm) is sufficiently smaller than a device area ( $4 \text{ mm}^2$ ).<sup>8</sup> The  $\epsilon_r$  of  $\alpha$ -NPD is determined to be  $3.42 \pm 0.02$  by measuring capacitance of  $\alpha$ -NPD sandwiched between Al using a 4284A LCR meter (Agilent) (the capacitance remains constant in a frequency range from 20 Hz to 100 kHz). The  $J$ - $V$  curves in the  $X$  range from 0.25 to 10 nm and at the specific  $Y$  of 0.75 nm are fitted using Eq. (1) with the common  $\mu_0$  of  $(7.8 \pm 0.5) \times 10^{-5} \text{ cm}^2/\text{V s}$  and  $\beta$  of  $(8.0 \pm 0.6) \times 10^{-4} \text{ cm}^{0.5}/\text{V}^{0.5}$  [Figs. 1(a) and 1(b)]. However, the obtained  $\mu_0$  is slightly lower than that measured by a time-of-flight (TOF) technique ( $\mu_0 = 4.0 \times 10^{-4} \text{ cm}^2/\text{V s}$  and  $\beta = 1.1 \times 10^{-3} \text{ cm}^{0.5}/\text{V}^{0.5}$ ).<sup>9</sup> It has been shown that hole mobilities of  $\alpha$ -NPD gradually increase and approach the TOF mobility with increasing its film thicknesses.<sup>4,10</sup> Thus, we infer that SCLC mobilities measured from thinner films become lower than TOF mobilities measured from thicker films.

Since there is an energy barrier of  $\approx 0.4 \text{ eV}$  at the ITO/ $\alpha$ -NPD interface,<sup>4</sup> holes must be injected across the barrier under a local high electric field [(A) in Fig. 2]. Hence, the  $J$ - $V$  curves at the  $X$  and the  $Y$  of 0 nm are controlled by an injection-limited current. On the other hand, we propose that a charge generation mechanism is more dominant than the charge injection mechanism when the  $\text{MoO}_2$  ( $\text{MoO}_3$ ) is used. First, charges are transferred from lower-ionization-potential (IP)  $\alpha$ -NPD to higher-work-function (WF)  $\text{MoO}_2$  ( $\text{MoO}_3$ ) to form electron-hole pairs [(B) in Fig. 2]. Second, the pairs are separated under an electric field and resultant electrons and holes move to the corresponding electrodes [(C) in Fig. 2]. The processes (B) and (C) are repeated for steady-state current flow. Under this situation, the injection barrier (A) is no longer considered important and the  $J$ - $V$  curves are controlled by the SCLC. The difference between the charge generation and the charge injection is whether the charge transfer occurs or not under no electric field.

To confirm the charge transfer, ultraviolet/visible/near-infrared (UV-vis-NIR) absorption spectra and fluorescence (FL) spectra of a 50 nm pure  $\alpha$ -NPD film and 50 nm composite films of  $\alpha$ -NPD: $\text{MoO}_2$  or  $\alpha$ -NPD: $\text{MoO}_3$  (1:1 by mol) are measured using V670 and FP-6500 spectrometers (JASCO), respectively. The original absorption peaks of  $\alpha$ -NPD at shorter wavelengths decrease in absorbance and the two absorption peaks appear at longer wavelengths by the mixing [Fig. 3(a)]. The longer-wavelength peaks originate from radical cations of  $\alpha$ -NPD generated by the charge transfer.<sup>11</sup> Due to quenching of  $\alpha$ -NPD excitons by the cat-

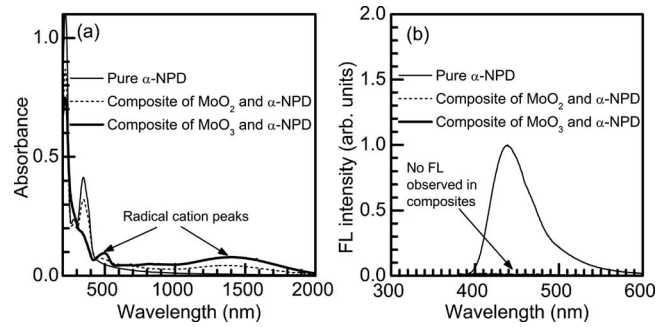


FIG. 3. (a) UV-vis-NIR absorption spectra and (b) FL spectra of pure  $\alpha$ -NPD film and composite films of  $\alpha$ -NPD: $\text{MoO}_2$  or  $\alpha$ -NPD: $\text{MoO}_3$ .

ions, the FL peaks completely disappear in the composites [Fig. 3(b)].

The charge transfer is also confirmed using multilayer structures [glass substrate/ITO (150 nm)/ $\text{MoO}_2$  ( $L$  nm) or  $\text{MoO}_3$  ( $M$  nm)/ $\alpha$ -NPD (5 nm), where  $L$  and  $M$  are changed from 0 to 10 nm]. A monochromatic excitation light (300 nm) is irradiated at  $45^\circ$  to obtain their FL spectra normal to the film plane using a PMA-11 analyzer (Hamamatsu) [Figs. 4(a) and 4(b)]. The FL intensities of  $\alpha$ -NPD at  $\approx 440 \text{ nm}$  decrease when the  $\text{MoO}_2$  ( $\text{MoO}_3$ ) is used, indicating that the charge transfer from  $\alpha$ -NPD to  $\text{MoO}_2$  ( $\text{MoO}_3$ ) surely occurs in the multilayer structures, which resemble the working device structures.

The FL intensities are plotted with  $L$  and  $M$  [Fig. 4(c)]. The FL intensities abruptly decrease in a thinner region ( $L < 1 \text{ nm}$  and  $M < 1 \text{ nm}$ ) and remain constant in a thicker region ( $L > 1 \text{ nm}$  and  $M > 1 \text{ nm}$ ). It has been shown from x-ray photoelectron spectroscopy that charge transfer from ITO to  $\text{MoO}_3$  occurs.<sup>4</sup> Thus, the smaller amount of  $\text{MoO}_2$  ( $\text{MoO}_3$ ) deposited on ITO and/or the charge transfer from ITO would make the charge transfer from  $\alpha$ -NPD less efficient, resulting in the intermediate FL intensities in the thinner region.

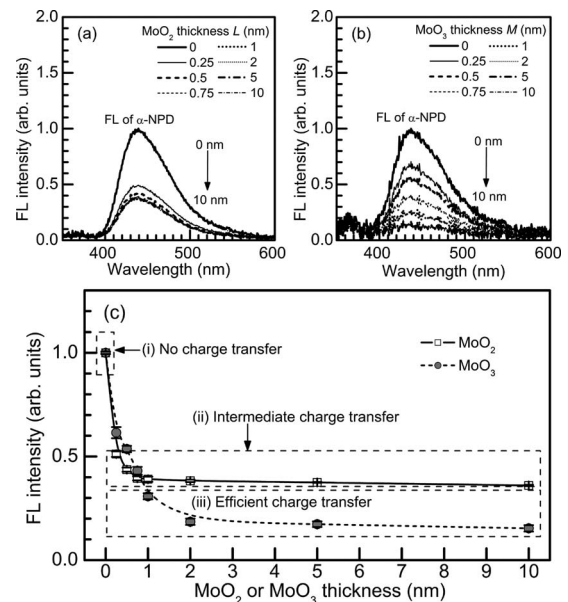


FIG. 4. FL spectra of  $\alpha$ -NPD on (a)  $L$  nm  $\text{MoO}_2$  and (b)  $M$  nm  $\text{MoO}_3$  ( $L$  and  $M$  are changed from 0 to 10 nm). (c) Changes in FL intensity of  $\alpha$ -NPD with  $L$  and  $M$ .

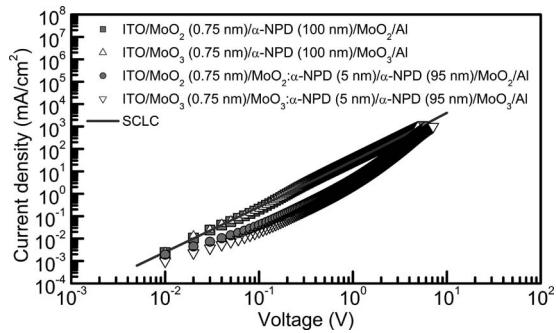


FIG. 5.  $J$ - $V$  characteristics of devices with multilayer and composite structures. Solid line represents SCLC.

Moreover, the FL intensities obtained using the  $\text{MoO}_3$  are lower than those obtained using the  $\text{MoO}_2$  in the thicker region, suggesting that the charge transfer from  $\alpha$ -NPD to  $\text{MoO}_3$  is more efficient than that from  $\alpha$ -NPD to  $\text{MoO}_2$ . This result agrees with the larger cation peaks observed in the  $\alpha$ -NPD: $\text{MoO}_3$  composite [Fig. 3(a)]. The more efficient  $\alpha$ -NPD-to- $\text{MoO}_3$  charge transfer can be explained by the larger difference between the IP of  $\alpha$ -NPD and the WF of  $\text{MoO}_3$  relative to the WF of  $\text{MoO}_2$  (see Fig. 2).

By using the  $\text{MoO}_2$  ( $\text{MoO}_3$ ), the charge injection mechanism [(A) in Fig. 2 and (i) in Fig. 4(c)] is mostly replaced with the charge generation mechanism [(B) and (C) in Fig. 2 and (ii) in Fig. 4(c)], resulting in the increase in  $J$  at the lower  $X$  and  $Y$ . In the region (ii), a hole generation rate would be almost equal to a hole transport rate of  $\alpha$ -NPD due to the intermediate charge transfer. Thus, the SCLC of  $\alpha$ -NPD is observed in this region. On the other hand, we speculate that a hole generation rate in the region (iii) is excessively higher than that in the region (ii) due to the most efficient charge transfer. Under this condition, the excess number of holes is generated and forms a strong space charge layer in  $\alpha$ -NPD, which may impede hole transport and induce the decrease in  $J$  at the higher  $Y$ .

To verify this hypothesis, the  $J$ - $V$  characteristics of the devices with the  $X$  and the  $Y$  of 0.75 nm are compared with those of devices [glass substrate/ITO (150 nm)/ $\text{MoO}_2$  or  $\text{MoO}_3$  (0.75 nm)/ $\alpha$ -NPD: $\text{MoO}_2$  or  $\alpha$ -NPD: $\text{MoO}_3$  (1:1 by mol) (5 nm)/ $\alpha$ -NPD (95 nm)/ $\text{MoO}_2$  or  $\text{MoO}_3$  (10 nm)/Al (100 nm)] (Fig. 5). The  $J$ - $V$  curves of the former two devices are similar and controlled by the SCLC in the wide  $V$  region from 0.01 to 5 V. However, the  $J$  of the latter two composite devices is lowered probably due to the excessively enhanced hole generation by improving contact between  $\alpha$ -NPD and  $\text{MoO}_2$  ( $\text{MoO}_3$ ) in the composite regions.

Transition metal oxides and alkali metals have been used as buffer layers and dopants in OLEDs.<sup>12–15</sup> Thicknesses and doping concentrations of these materials have been optimized to obtain the best performances (1 nm for  $\text{Fe}_3\text{O}_4$  as a  $p$ -type buffer layer,<sup>12</sup> 33% for  $\text{WO}_3$  as a  $p$ -type dopant,<sup>13</sup> <3 nm for Cs as a  $n$ -type buffer layer,<sup>14</sup> and 50% for Li as a  $n$ -type dopant<sup>15</sup>). However, use of the thicknesses and the concentrations beyond the optimized levels is known to increase the voltages.<sup>12–15</sup> The voltage increase is probably due to excessive charge generation similar to that observed here. The advantage when using the  $\text{MoO}_2$  is that the suitable charge generation is obtained and that the SCLC is observed in the wide  $X$  range when compared with  $\text{MoO}_3$ . Finally, we emphasize that it is important to control the charge generation rates by adjusting the thicknesses, the concentrations, and the materials with different WF.

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