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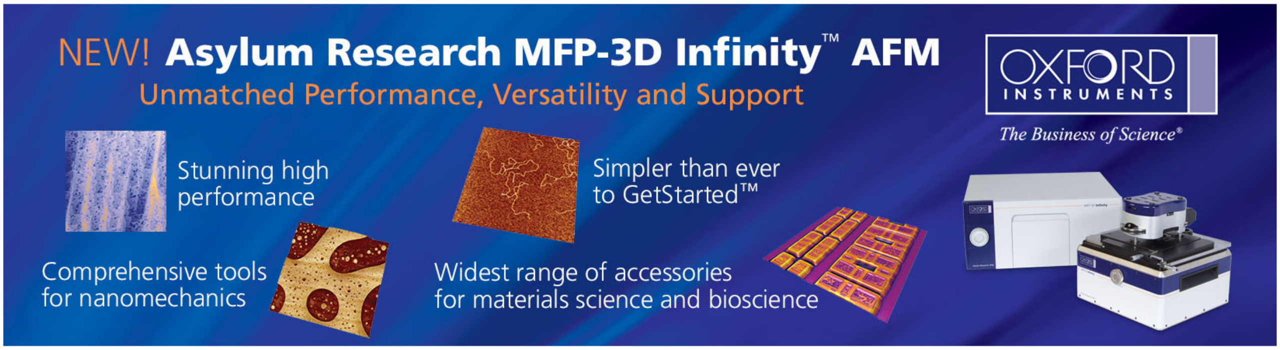

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Study of electrical characterization of 2-methyl-9,10-*di*(2-naphthyl)anthracene doped with tungsten oxide as hole-transport layer

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An efficient *p*-doped transport layer composed of an ambipolar material, 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) and tungsten oxide (WO_3) has been developed. The admittance spectroscopy studies show that the incorporation of WO_3 into MADN can greatly improve the hole injection and the conductivity of the device. Moreover, when this *p*-doped layer was incorporated in the tris(8-quinolinolato)aluminum-based device, it achieved a current efficiency of 4.0 cd/A and a power efficiency of 2.4 lm/W at 20 mA/cm^2. This work paves the way to simplify the fabrication of future *p*-*i*-*n* organic light-emitting devices with a single common ambipolar MADN material. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3173824]

Since the efficient organic light-emitting devices (OLEDs) were discovered, developing OLEDs for various applications has attracted much attention.[1,2] However, the intrinsic properties of organic materials limit the development of OLEDs, such as the low power efficiency and high driving voltage. In order to achieve the OLEDs with low driving voltage and high power efficiency for commercial applications, electrical doping is commonly adopted in OLEDs due to that highly conductive *p*- and *n*-doped layers could enhance the carrier injection from the contacts and reduce the Ohmic losses in these layers.[3–10] Recently, one of the most commonly used *n*-type dopants, cesium carbonate, has been reported by Canon Inc. to facilitate electron injection from a wide range of metal electrodes.[11] On the anode side, our group has developed tungsten oxide (WO_3) as an efficient *p*-type dopant for a hole transporting layer (HTL),[12] which exhibits very good hole-injection properties.

In our previous work, 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) has been shown to be an efficient blue host material which forms a stable thin-film morphology upon thermal evaporation and also has a wide energy band gap.[13] Moreover, the charge transporting properties of MADN was examined further in the form of amorphous films as functions of electric field and temperature by means of time-of-flight (TOF) technique.[14,15] By TOF measurements, MADN was discovered to exhibit an ambipolar transporting property, the values of electron and hole mobilities of MADN have been measured to be $(2-3) \times 10^{-7}$ cm^2/V s, respectively.[16] Lee also developed a *n*-type electron transport layer (ETL) by doping cesium fluoride into MADN and found that this *n*-type ETL is capable of lowering the driving voltage and enhancing the efficiency of OLED devices.[17] In this paper, we report the development of the *p*-doped transport layers using the ambipolar host MADN in a tris(8-quinolinolato)aluminum (Alq_3) based device, in which WO_3 is served as *p* dopant. Their carrier injection properties and the effect of WO_3 incorporation into MADN were studied by current-voltage (I-V) correlation and temperature-dependent admittance spectroscopy measurements. The result demonstrates that the incorporation of WO_3 into MADN can reduce the resistance and activation energy of MADN layer, which in turn reduces energy barrier of hole injection from indium tin oxide (ITO) anode to MADN layer and Ohmic loss of the device. Moreover, the electrochemical property of MADN was also investigated by cyclic voltammetry (CV). As shown in Fig. 1, MADN shows a reversible and stable oxidation peak even after multiple scans by using 0.1M tetrabutylammonium hexafluorophosphat as the supporting electrolyte in dichloromethane. This result suggests that MADN possesses a stable oxidation state and is capable of generating free holes in the presence of WO_3 as *p*-type dopant.

A series of hole-only devices were fabricated for studying the effect of hole injection and electrical characteristics. The hole-only device structure was ITO/*p*-doped HTL (60 nm)/Alq_3 (60 nm)/aluminum (Al)(150 nm), in which the doping volume percentage of WO_3 in MADN as *p*-doped HTL were 0%, 10%, 20%, and 33%, respectively. Further-

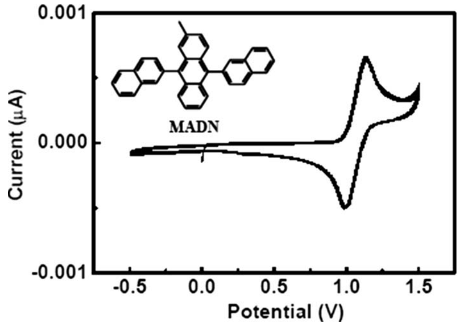

FIG. 1. Repeated scan (100 times) of cyclic voltammograms and the chemical structure of MADN.

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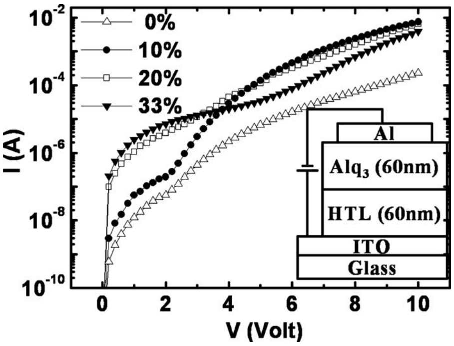

FIG. 2. (*I-V*) characteristics of hole-only devices with 0%, 10%, 20%, and 33% WO$_3$-doped MADN at room temperature. Inset: The structure of hole-only device.

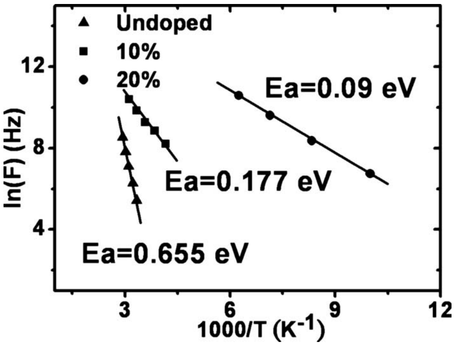

FIG. 4. Plots of $\ln(F)$ vs $1000/T$. The F is derived from the low-frequency peak in the G/F-F spectra.

more, we fabricated the OLEDs devices with the same *p*-doped HTL, whose structure was ITO/*p*-type HTL (50 nm)/MADN (10 nm)/Alq$_3$ (75 nm)/LiF (1 nm)/Al (150 nm). The doping volume percentage of WO$_3$ for devices A, B, C, and D are 0%, 10%, 20%, and 33%, respectively.

Figure 2 plots the *I-V* characteristics of the hole-only devices. It is shown that the WO$_3$-doped hole-only devices all greatly outperform the undoped device, indicating that doping WO$_3$ into MADN promotes the injection of hole from ITO anode. At a small applied bias, the device with 33% WO$_3$ has the best *I-V* characteristics than most of the other WO$_3$-doped devices. At a high applied bias, however, the device with 10% WO$_3$ outperforms the hole-only devices. To understand the phenomena, the hole-only devices are further investigated by admittance spectroscopy, as shown in Fig. 3. In order to compare the effects of WO$_3$ doped into MADN for various doping percentages clearly, the spectrum measured at 300 K is boldfaced. Based on the theory of admittance spectroscopy with an equivalent circuit model of the heterojunction hole-only device,[18] the low-frequency peak (temperature-dependent) in Fig. 3 is assigned to be associated with a single resistance-capacitance (RC) time constant of the MADN layer and high-frequency peak (temperature-independent) is associated with a single RC time constant of parasitic series resistance.[19] In Fig. 3, as WO$_3$ percentage is increased, the MADN peak shifts gradually toward the high frequency region and finally mixes with the series resistance peak (see the spectrum measured at 300 K), indicating that doping WO$_3$ into MADN can greatly reduce the resistance of MADN layer according to the relationship of $2\pi F=(RC)^{-1}$. Furthermore, according to the temperature-dependent peaks, the activation energies (E_a) of MADN layer for various doping percentages can be obtained by the relationship of $F=F_0 \exp[(-E_a)/(KT)]$ (where F_0 is the pre-exponential factor, K is Boltzmann's constant, and T is the temperature) and are shown in plots of $\ln(F)$ versus $1000/T$ in Fig. 4. As shown, when the doping percentage of WO$_3$ is increased from 0% to 10% and then to 20%, the E_a of MADN could be greatly reduced from 0.655 to 0.177 eV and then to 0.09 eV. However, as the doping percentage further increases to 33%, the MADN peak still cannot be resolved from the series resistance peak even at a temperature of 78 K. As a result, the E_a cannot be obtained exactly, but it could be estimated to be less than 0.09 eV. Owing to that, the E_a represents the energy separation between the edge of the highest occupied molecular orbital and Fermi level, the decrease of E_a indicates that the WO$_3$ incorporation reduces this separation resulting in decreasing the width of the hole injection energy barrier between MADN and ITO, suggesting that the hole injection from ITO to MADN layer could be improved. The improvement can be demonstrated in Fig. 1, where the room-temperature *I-V* characteristics of the hole-only devices in logarithm scale are plotted. As is shown, the current is gradually improved from the undoped device to the device doped with 33% WO$_3$ at a small applied bias which agrees with the results concluded from Fig. 4 because the current condition of the hole-only device at the small applied bias is mainly dominated by hole injection from ITO to HTL layer. Therefore, the enhanced current condition at the small applied bias can be ascribed to the reduced width of energy barrier between MADN and ITO. At the high applied bias, however, the device doped with 10% WO$_3$ outperforms the other devices, suggesting that the hole injection barrier becomes negligible at the high applied bias, thus it is likely that the current conduction is dominated by the carrier transport in the bulk of hole-only device. In a heavy doping percentage, the WO$_3$ could be diffused into the Alq$_3$ layer resulting in creating the trap center near the interface between MADN and Alq$_3$ which limits the carrier transport via the interface between MADN and Alq$_3$. As a result, the device doped with 33% shows a worse current condition than that of the devices doped with 10% and 20% at the high applied bias. Following this study, we conclude that the *p*-doped HTL of MADN doped with WO$_3$ is expected to improve hole injection and reduce Ohmic loss in OLED devices.

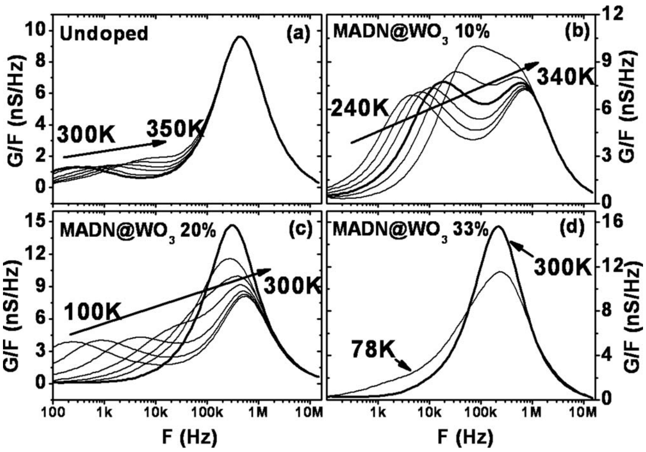

FIG. 3. Temperature-dependent G/F-F spectra at zero bias for hole-only devices doped with (a) 0%, (b) 10%, (c) 20%, and (d) 33% WO$_3$.

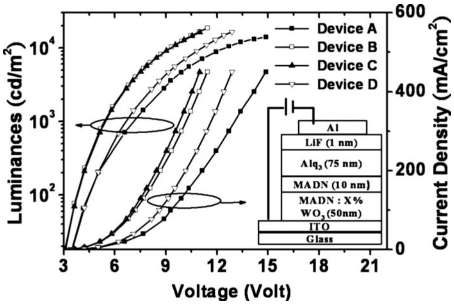

FIG. 5. (*L*-*J*-*V*) curves of devices A, B, C, and D. The structure is shown in the inset.

Figure 5 shows the luminance-current density-voltage (*L*-*J*-*V*) relationship of devices A–D. Compared to the device A, higher current density and luminance can be achieved at lower applied bias by using WO_3 as *p* dopant. The overall electroluminescence (EL) performances of these devices are summarized in Table I. Device B achieved a power efficiency of 2.4 lm/W at 20 mA/cm^2, which is 43% higher than that of undoped device A. The results in Table I show excellent agreement with the conclusions obtained from the study of hole-only device and clearly dominant that the MADN doped with WO_3 could be adopted for an efficient HTL in OLEDs device.

In summary, we demonstrated that the MADN doped with WO_3 decreases the resistance of MADN and the hole injection energy barrier between MADN and ITO resulting in improving the Ohmic loss and hole injection. In Alq_3 based OLEDs, using MADN doped with WO_3 as HTL can achieve a current efficiency of 4.0 cd/A and a power efficiency of 2.4 lm/W. Furthermore, by taking the advantage of the ambipolar property of MADN, we believe that it is possible to construct power efficient OLEDs using MADN as hosts for both the *p*-doped HTL and the *n*-doped ETL, thus paving the way for fabricating a much simplified *p*-*i*-*n* OLEDs device using a common host material not only for RGB emitters but for electron and hole transport layers as well.

TABLE I. EL performance of devices with various doping percentages driven at 20 mA/cm^2.

Device	Voltage (V)	Luminance (cd/m^2)	Yield (cd/A)	Power efficiency (lm/W)
A	6.6	707	3.5	1.7
B	5.2	790	4.0	2.4
C	5.1	711	3.6	2.2
D	6.2	692	3.5	1.8

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