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Highly power efficient organic light-emitting diodes with a *p*-doping layer

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In this letter, the authors demonstrate *p-i-n* organic light-emitting diodes (OLEDs) incorporating a *p*-doped transport layer which comprises tungsten oxide (WO_3) and $4,4',4''$-tris(*N*-(2-naphthyl)-*N*-phenyl-amino)triphenylamine (2-TNATA) to replace the volatile tetrafluro-tetracyano-quinodimethane. The authors propose the 2-TNATA:WO_3 composition functions as a *p*-doping layer which significantly improves hole injection and conductivity of the device that leads to the fabrication of tris(8-quinolinolato)aluminum based *p-i-n* OLEDs with long lifetime, low driving voltage (3.1 V), and high power efficiency (3.5 lm/W) at 100 cd/m². © *2006 American Institute of Physics*. [DOI: 10.1063/1.2405856]

Since the efficient organic light-emitting devices (OLEDs) have been discovered, there has been considerable interest in developing OLEDs with high efficiency and long lifetime for display applications.[1,2] In order to lower power consumption and driving voltage, it is critical to enhance the carrier injection from the electrode to the transporting layer and to increase the transport conductivity.[3,4] Recently, the *p*-doping hole-transporting layer (HTL) for enhancing carrier injection and lowering drive voltages in OLEDs has attracted a lot of attention. The *p*-doping HTL is typically made by coevaporating the hole-transporting material with a strong electron acceptor such as tetrafluro-tetracyano-quinodimethane (F4-TCNQ),[5] or oxidants such as antimony pentachloride ($SbCl_5$),[6] ferric chloride ($FeCl_3$),[7] and iodine.[8] It appears that *p* doping not only reduces the Ohmic loss in HTL but also improves hole injection by tunneling.[9] However, the use of highly volatile F4-TCNQ as *p*-type dopant in thermal evaporation under high vacuum has raised serious concerns over issues of cross contamination, chamber pollution, and the thermal stability of OLEDs.

In this study, an inorganic electron acceptor, i.e., tungsten oxide (WO_3), was coevaporated with $4,4',4''$-tris(*N*-(2-naphthyl)-*N*-phenyl-amino)triphenylamine (2-TNATA) to form a *p*-doping HTL in tris(8-quinolinolato)aluminum (Alq_3) emitter devices with the motive to replace the highly volatile F4-TCNQ. We demonstrate a *p-i-n* OLED by incorporating this *p*-doped HTL with *n*-doping bathophenanthroline (BPhen):cesium (Cs) to enhance the electron injection in this system which produced a power efficiency of 3 lm/W (20 mA/cm²) at 4 V that is among the best reported for Alq_3 based emitter.

The UV-vis-NIR absorption spectra of 200 nm thick 2-TNATA, WO_3, and 2-TNATA:WO_3 films on the quartz substrates are shown in Fig. 1. The absorptions of pure 2-TNATA and WO_3 film are all located at the wavelength less than 400 nm, while the 2-TNATA:WO_3 film revealed absorption peaks at around 800 and 1400 nm, which is attributed to that WO_3 can accept electron from 2-TNATA to

form charge-transfer complex (WO_3^-/2-TNATA$^+$).[6,10] The NIR absorption demonstrates that the WO_3 is also capable of accepting electron from 2-TNATA to generate free holes in these doping films.

For the study of hole injection and transporting ability of 2-TNATA:WO_3 films, a series of hole-only devices of indium tin oxide (ITO)/2-TNATA:x%WO_3 (100 nm)/ $1,4$-*bis*[*N*-(1-naphthyl)-*N'*-phenylamino]–$4,4'$ diamine (NPB) (60 nm)/aluminum (Al) (150 nm) was fabricated. The schematics are depicted as insets in Fig. 2. Detail of the fabrication process can be found elsewhere.[11,12] The *J-V* characteristics at various doping ratios of WO_3 to 2-TNATA are shown in Fig. 2. Increasing the WO_3 volume percentage from 0% to 33% enhances the current conduction gradually which is due to the decrease of the resistance and activation energy of the doping layer.[12] However, the current conduction is reduced slightly as the doping ratio further increases to 50%. This result may be attributed to the effect of carrier quench and generation of defects.

The *p-i-i* and *p-i-n* devices with Alq_3 emitter have also been fabricated for comparison. The device structures are depicted as the insets in Fig. 3 where NPB, Alq_3, and BPhen were used as the electron-blocking material, light-emitting material, and hole-blocking material, respec-
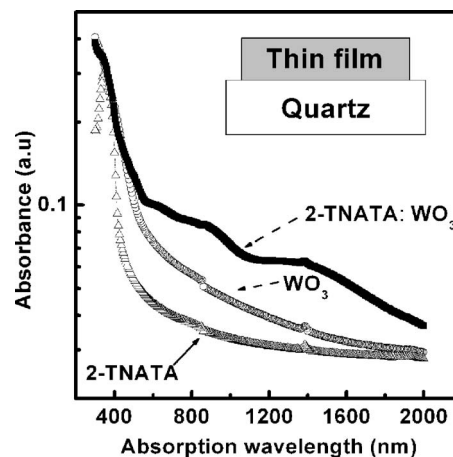

FIG. 1. Absorption spectra of pure and WO_3 doped 2-TNATA thin films.

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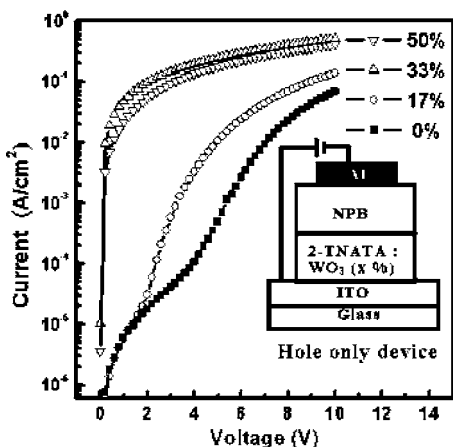b)Author to whom correspondence should be addressed; electronic mail: mthsieh.ep94g@nctu.edu.tw

FIG. 2. Current vs voltage characteristics of hole-only devices with 0%, 17%, 33%, and 50% WO$_3$ doped 2-TNATA films. Inset: The structure of hole-only devices.

tively. A *p-i-i* multiplayer structure of 2-TNATA: WO$_3$/NPB/Alq$_3$/lithium fluoride (LiF)/Al was deposited on the ITO substrate by resistive heating with thicknesses of 100, 10, 60, 1, and 150 nm for 2-TNATA:WO$_3$, NPB, Alq$_3$, LiF, and Al, respectively. In the *p-i-i* devices with 100 nm thick 2-TNATA:WO$_3$ layer, the WO$_3$ volume percentages are 0%, 17%, 33%, and 50% for devices A, B, C, and D, respectively. The voltage and power efficiency of the *p-i-i* devices with various doping ratios of WO$_3$ at current density of 20 mA/cm^2 are shown in Fig. 3. The driving voltage is reduced dramatically when WO$_3$ is doped in 2-TNATA. This trend is consistent with the current enhancement for a doping ratio up to 33%, which shows that the current conductions of *p-i-i* devices and hole-only devices are mainly both dominated by the hole-injection layer. However, when the doping ratio increases to 50%, Fig. 3 shows an inconsistency with the hole-only device, probably due to the effects of cathode (LiF/Al) and the NPB/Alq$_3$ interface. Furthermore, the voltage and power efficiency characteristics are highly dependent on the doping ratio of WO$_3$. The devices with WO$_3$ doped 2-TNATA layer are able to generate a substantially larger current density and electroluminescence (EL) output at the same forward drive voltage than the nondoped devices. However, the maximum power efficiency of the devices with a doping ratio of 17%, 2.4 lm/W (corresponding to the high-

est luminous efficiency of about 4.4 cd/A) at 20 mA/cm^2, is higher than that of these devices with doping ratios of 0%, 33%, and 50%, which are about 2.1, 2.3, and 1.3 lm/W (corresponding to the luminous efficiencies of about 4.3, 4.2, and 2.2 cd/A) at 20 mA/cm^2, respectively. The lowest voltage was observed at the maximal ratio of 50% in device D, however, at the expense of power efficiency. The reason can be attributed to unbalanced hole/electron recombination in the emission layer of OLEDs. These results clearly demonstrate that hole injection has been enhanced due to the *p*-doping 2-TNATA:WO$_3$ layer. We also found that the *p-i-i* devices with or without O$_2$ plasma treatment on ITO surface exhibited the same current density versus voltage (*J-V*) characteristics, meaning that the hole-injection barrier was eliminated.

To balance the enhanced hole injection with the *p*-doping 2-TNATA:WO$_3$ layer, a *n*-doping BPhen:2% Cs layer was incorporated in device E to enhance the balance of electron and hole. The structure of the *p-i-n* device E is [ITO/2-TNATA:33% WO$_3$ (100 nm)/NPB (10 nm)/Alq$_3$ (30 nm)/Bphen (20 nm)/BPhen:2% Cs (10 nm)/Al (150 nm)]. Figure 4 and the inset show the *J-V* and power efficiency versus luminance characteristics of these EL devices, respectively. Compared to nondoped device A, higher current density can be reached at lower voltage by using *p-i-n* architecture in device E. Higher power efficiency than that of *p-i-i* device C was observed in device E, which is attributed to the enhancement of the electron injection from cathode resulting in the electron/hole balance. The overall EL performances of these devices are summarized in Table I. The luminous efficiency of device E with WO$_3$ as inorganic electron-acceptor dopant can be improved to 4.5 cd/A with a power efficiency of 3 lm/W (20 mA/cm^2) at 4 V that is

FIG. 4. Current density vs voltage of Alq$_3$ devices. Inset: Power efficiency vs luminance characteristics.
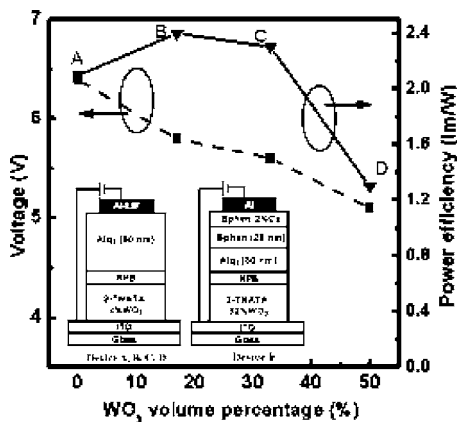

FIG. 3. Voltage and power efficiency vs doping ratio characteristics of device A (undoped), device B (17%), device C (33%), and device D (50%) at 20 mA/cm^2. Inset: The structures of *p-i-i* and *p-i-n* devices with Alq$_3$ emitter.
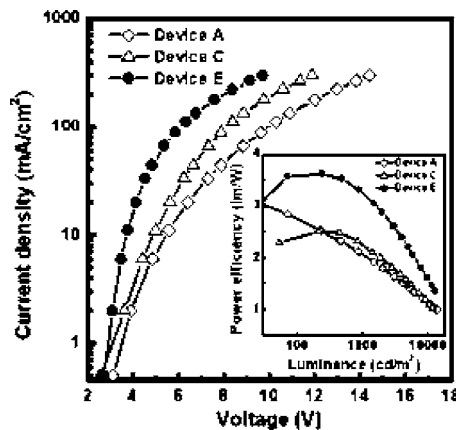
TABLE I. EL performance of devices with different structures driven at 20 mA/cm^2.

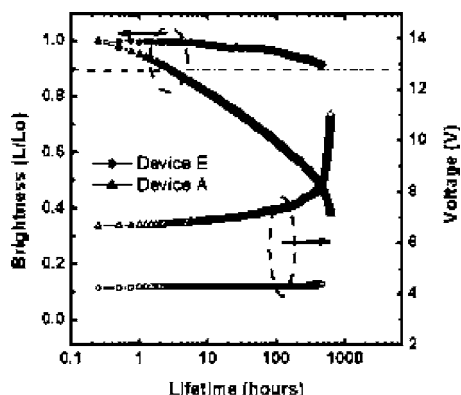|	Device		
	A (Undoped)	C (*p–i–i*)	E (*p–i–n*)
Operating voltage (V) for 100 cd/m^2	4.2	4.0	3.1
Driving voltage (V) for 20 mA/cm^2	6.4	5.6	4.1
Power efficiency (lm/W) for 20 mA/cm^2	2.1	2.3	3.3
Current efficiency (cd/A) for 20 mA/cm^2	4.3	4.1	4.4

FIG. 5. Operational stability of two OLEDs driven at room temperature under constant current density of 20 mA/cm^2.

comparable to the best ever reported for an Alq$_3$ emitter.

The lifetimes of the encapsulated devices A and E were examined under the condition of a constant current device density of 20 mA/cm^2 in ambient for comparison, and the result is shown in Fig. 5. Device E shows a lifetime with a t_{90} exceeding 700 h, which is an order of magnitude higher than that of the nondoped device A. Besides, the driving voltage of device E is also more stable than that of device A.

Hole injection is considered to be one of the most important factors that dictate the driving voltage of OLEDs. In this letter, we use WO$_3$ as inorganic metal oxide for the electron-acceptor dopant in HTL to fabricate p-i-n devices. We find that WO$_3$ is more thermally stable, cost effective, and easily available than the highly volatile and contaminat-

ing organic dopant F4-TCNQ. We have also demonstrated the long lifetime, low driving voltage (3.1 V), and high power efficiency (3.5 lm/W) at 100 cd/m^2 in Alq$_3$ based p-i-n OLEDs. From these results, we strongly believe that our p-doping layer can improve the hole injection and would be a viable replacement dopant material for F4-TCNQ in robust p-i-n devices.

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