

Air stable and low temperature evaporable Li_3N as a n type dopant in organic light-emitting diodes

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ABSTRACT

N doped organic light-emitting diodes were developed by using Li_3N as a n type dopant in electron transport layer. Driving voltage was greatly lowered by using Li_3N doped electron transport layer and combination of MoO_3 doped hole transport layer with Li_3N doped electron transport layer gave high quantum efficiency of 15% and low driving voltage of 4 V at 1000 cd/m^2 in green phosphorescent organic light-emitting diodes. Decomposition of Li_3N during evaporation into Li and N_2 was found to be responsible for n doping effect of Li_3N .

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1. Introduction

Organic light-emitting diodes (OLEDs) have been widely applied as a display in mobile appliances and they can be used in large size display such as monitors and television. However, power consumption of OLEDs needs to be improved further to expand their applications.

There have been many studies to improve the power consumption of OLEDs and most studies focused on reducing the driving voltage of OLEDs. The most effective way to reduce the driving voltage of OLEDs is to use p type and n type doping structure in charge transport layers [1–4]. Various p type doping materials based on organic or inorganic materials have been developed. 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($\text{F}_4\text{-TCNQ}$) is a well known p type dopant and it was effective to lower the driving voltage of OLEDs [5,6]. Inorganic oxide based doping materials were also reported and WO_3 , MoO_3 , and V_2O_5 could reduce the driving voltage by doping in aromatic amine type hole transport materials [7–9].

Even though many p type doping materials have been reported, n type doping materials are limited and only a few n type doping materials have been developed [10,11]. Li and Cs are representative n type doping materials and they could give driving voltage lower

than 4 V at 1000 cd/m^2 by combination with p doped hole transport layer. Other than Li and Cs, Cs_2CO_3 could play a role of n type dopant by evaporation and solution process [12]. However, these n doping materials suffer from a high evaporation temperature and an unstable evaporation process because they are unstable in air. Therefore, a n doping material with a low deposition temperature and stable operation in air should be developed.

In this work, Li_3N was developed as a n doping material in the electron transport layer because Li_3N can be decomposed into Li during evaporation and it can be deposited at a low deposition temperature. Its deposition behavior and device performances of Li_3N doped OLEDs were investigated in this work.

2. Experimental

Standard device structure used in this experiment was indium tin oxide (ITO, 150 nm)/N, N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB, 60 nm)/4,4',4''-tris(N-carbazolyl)triphenylamine (TCTA, 10 nm)/TCTA: 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBI): tris(2-phenylpyridine) iridium ($\text{Ir}(\text{ppy})_3$) (30 nm, 5% doping)/4,7-diphenyl-1,10-phenanthroline (Bphen, 30 nm)/LiF (1 nm)/Al (200 nm). Li_3N doped devices had Bphen (10 nm)/Bphen: Li_3N (20 nm, 30%) layer instead of Bphen/LiF layer. Al was directly deposited on Bphen: Li_3N layer without LiF. MoO_3 doped NPB layer (10 nm, 30%) was used as a hole transport layer to further reduce the driving voltage of Li_3N doped devices. Device structures used in this work are shown in Fig. 1. Single layer devices of

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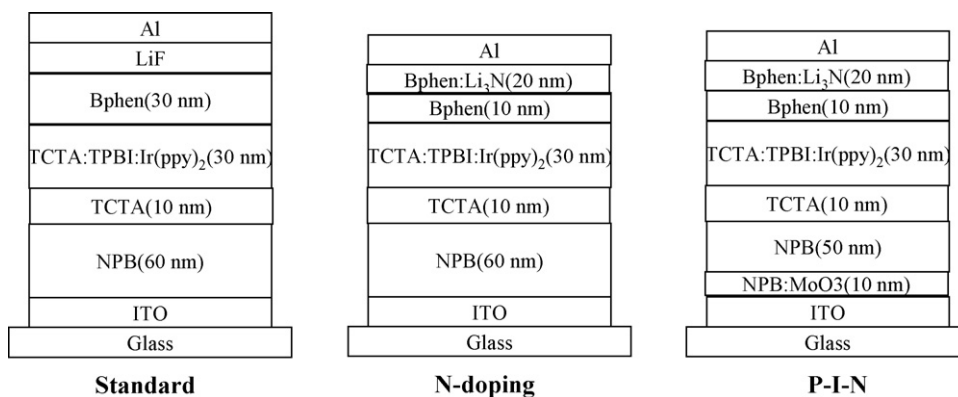


Fig. 1. Device structures of phosphorescent organic light-emitting devices used in this work.

ITO/Bphen:Li₃N (100 nm)/Al were also fabricated to study the electron injection behavior of Li₃N doped Bphen layer. Current density–voltage–luminance characteristics of the devices were measured with Keithley 2400 source measurement unit and CS 1000 spectrophotometer. X-ray photoelectron spectroscopy was used for the analysis of doping mechanism of Li₃N.

3. Results and discussion

It is well known that Li and Cs have n type doping effect when they are combined with electron transport materials such as Bphen [13]. Even though they show superior performances as a n type dopant with Bphen, deposition temperature is high and doping control is difficult because they are sensitive to moisture or oxygen. Therefore, n type doping materials with a low deposition temperature and with process stability have to be developed and Li₃N was developed as a n dopant to impart n doping effect with Bphen. Li₃N has been known to decompose into Li and N₂ at high temperature [14] and only Li can be deposited on substrate during deposition. Inert N₂ formation during evaporation is not harmful to device performances compared with Cs₂CO₃ which gives off CO₂ during evaporation [12]. In addition, deposition temperature of Li₃N is similar to that of aromatic amine materials and it can be evaporated in common organic sources. Therefore, it can be effective as a n type doping material with Bphen and is expected to give a low driving voltage in OLEDs.

The decomposition mechanism of Li₃N was studied using XPS to confirm the thermal decomposition of Li₃N during evaporation. Quartz crystal after Li₃N deposition was analyzed to prove Li deposition on substrate and wide scan XPS spectra of Li₃N deposited quartz crystal are shown in Fig. 2. Investigation of Li_{1s} and N_{1s} peaks gives information about the mechanism for n doping effect of Li₃N and it is expected that N_{1s} peak may not be detected in XPS spectra if Li₃N is decomposed into Li and N₂. In XPS spectra of quartz crystal

with Li₃N film, Li_{1s} peak was clearly detected at 54.0 eV and 62.0 eV, while N_{1s} peak was not observed as can be seen in Fig. 2. N_{1s} peak should be observed around 400 eV, but no peak was observed in XPS spectra of quartz crystal, indicating that only Li was deposited on substrate. Therefore, it can be concluded that Li doping can be easily induced by thermal evaporation of Li₃N due to the decomposition of Li₃N during evaporation.

The n type doping effect of Li may induce an ohmic contact between electrodes and Li₃N doped Bphen layer. Single layer devices of ITO/Bphen:Li₃N/Al were fabricated and the current density–voltage characteristics were measured. Fig. 3 shows device data of single layer devices according to doping concentration of Li₃N. The single layer devices showed a linear relationship between the current density and voltage, indicating an ohmic contact of Li₃N doped Bphen layer with ITO and Al. From the current density–voltage relationship, the conductivity of the Li₃N doped Bphen layer was calculated. The conductivity of the Li₃N doped Bphen layer was gradually increased by doping and a conductivity of 10^{−6} S/cm order was obtained. From these results, it can be expected that Li₃N doping can improve the electron injection due to ohmic contact with Al cathode and high bulk conductivity of the Li₃N doped Bphen layer.

Device performances of Li₃N doped devices were investigated by fabricating three different devices in Fig. 1. Current density–voltage–luminance characteristics of devices are shown in Fig. 4. Current density of Li₃N doped device was greatly improved compared with that of standard device, implying strong n doping effect of Li₃N with Bphen. The current density was further increased by MoO₃ doping in NPB. Luminance also showed similar trend because luminance is high in the device with high current density. Li doping effect with Bphen is already well known [13] and Li doping by Li₃N deposition enhanced the current density of Li₃N

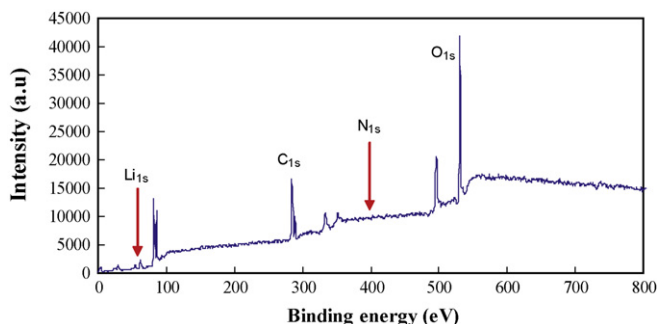


Fig. 2. XPS spectra of Li₃N films evaporated on quartz crystal.

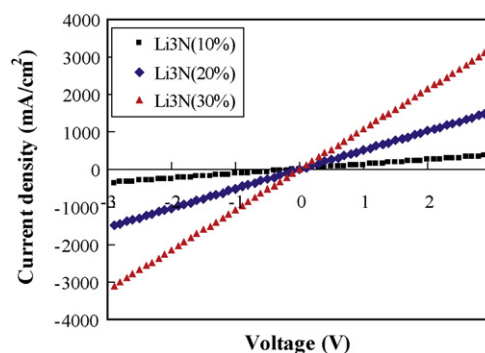


Fig. 3. Current density–voltage curves of the single layer devices of ITO/Bphen:Li₃N/Al according to Li₃N doping concentration.

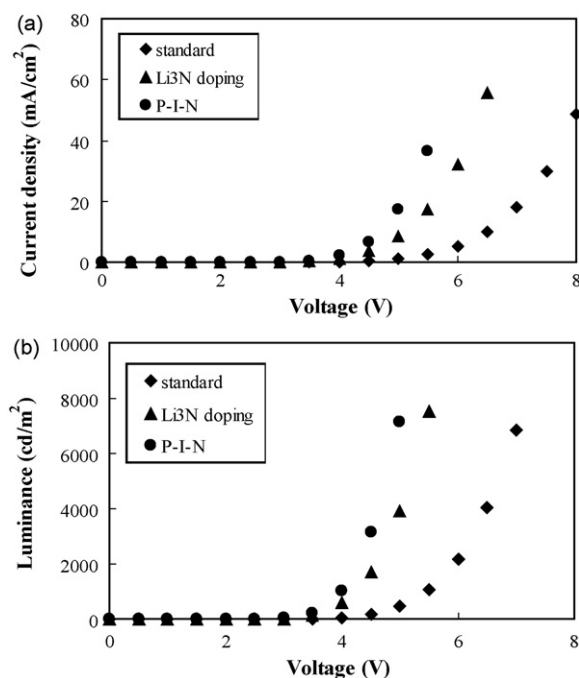


Fig. 4. Current density–voltage–luminance curves of green phosphorescent devices with Li₃N doped electron transport layer. (a) Current density–voltage and (b) current density–luminance.

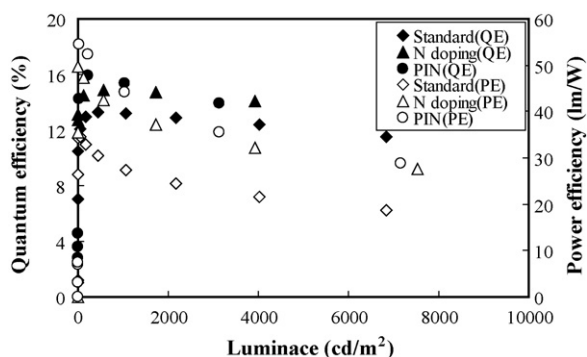


Fig. 5. Quantum efficiency and power efficiency of green phosphorescent devices with Li₃N doped electron transport layer.

doped devices. As explained in Fig. 3, the ohmic contact and the high conductivity of Li₃N doped Bphen layer facilitated electron injection and transport in the device. The driving voltage of the standard device at 1000 cd/m² was 5.4 V, but it was reduced by more than 1 V by using the Li₃N doped Bphen electron transport layer. p type doping of MoO₃ in NPB further decreased the driving voltage of the green phosphorescent OLEDs and a low driving voltage of 3.9 V was obtained in the p-i-n device.

Quantum efficiency and power efficiency of Li₃N doped devices were plotted against luminance and it is shown in Fig. 5. Quantum efficiency of Li₃N doped device was quite similar to that of standard device and high quantum efficiency of 15% was obtained in the device with p-i-n structure. The high quantum efficiency in Li₃N doped device indicates that Li₃N doping does not have any negative effect on light-emitting efficiency through exciton quenching or charge unbalance. Charges can be confined in the mixed host emitting structure used in this work [15] and high quantum efficiency could be obtained. Power efficiency of Li₃N doped devices could be enhanced due to the low driving voltage and a high quantum efficiency. The power efficiency at 1000 cd/m² was 44 lm/W compared with 27 lm/W of standard device.

4. Conclusions

In summary, Li₃N could be effectively used as a n type dopant with Bphen and driving voltage could be reduced by more than 1.5 V at 1000 cd/m². High quantum efficiency of 15% and high power efficiency of 44 lm/W were obtained in Li₃N doped device when Li₃N doped layer was combined with MoO₃ doped NPB layer. Li₃N could be stably deposited at a temperature range of organic materials and it was quite stable even after exposure to air. Therefore, it is expected that n type doping structure can be widely used in future OLED applications.

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