Hole Transfer Layer p-doped with a Metal Oxide for Low Voltage Operation of OLEDs

Won-Ju Shin[1], Je-Yun Lee, Jae-Chang Kim, and Tae-Hoon Yoon
[1]School of Electrical Engineering, Pusan National University, Busan, Korea
TEL:82-51-510-1700, e-mail: wenju@pusan.ac.kr
Tae-Shick Kim and Ok-Keun Song[2]
[2]R&D Center, Samsung SDI, Giheung-gu, Yongin, Gyeonggi-do 449-577, Korea

Keywords : metal oxide, p-dopant, charge transfer complex, life-time

Abstract
V_2O_5 was tested as a p-dopant for lower operating voltage and higher stability of OLEDs. Low voltage and high stability were achieved using this doping layer. It can be separated to bulk and interface contributions and the latter is a more dominant factor both of operation voltage and stability.

1. Introduction

The performance of OLEDs is good enough to be adopted in mobile applications or other devices commercially but its power consumption and operating life-time are still critical issues. Both are not equal but strongly dependent on each other so it is very important to achieve higher power efficiency of OLEDs by development of more efficient materials and structures. Higher power efficiency can be realized by achieving higher external quantum efficiency and lower operating voltage.

It has been known that doping in transfer layers is an effective method for the reduction of injection barrier and for achieving high conductivity that can promise lower operating voltage of OLEDs. Alkali metals or cationic dyes were used as n-type dopant in the electron transfer layer. Many p-dopant materials, such as F4-TCNQ,[1] $FeCl_3$,[2] $SbCl_5$,[3] have been reported to have very strong electron accepting characteristics. However, these doping materials can contaminate the vacuum chamber and other materials in the same chamber.

In this study, metal oxide is tested as a p-dopant in host NPB as HTL to achieve low operation voltage of OLEDs without any contamination problem. To study both effects on interface and bulk properties, the thickness of doped layer in OLEDs was varied whereas the total thickness of HTL from ITO to emission layer was fixed by insertion of pure NPB.

2. Experimental

At first, we make certain the fact that transition metal oxide is good as a p-dopant by confirming the optical and electrical characteristics of V_2O_5 doped NPB single layers with various doping concentrations. And then we introduce the layer to common green OLEDs which are characterized to verify the doping effects on operation voltage and stability.

All devices used in this work were fabricated on ITO coated-glass with a sheet resistance of 15 Ω/□. Active area of devices was 4 mm^2. After routine cleaning process of the ITO substrate, and then it was cleaned with the detergent, isopropanol, and deionized water subsequently. Oxygen plasma treatment was used to remove excess moisture on the substrate. To fabricate the doped layer, V_2O_5 and NPB were co-evaporated from separated sources in the same chamber. Un-doped NPB and Alq_3 were subsequently deposited by conventional thermal evaporation at the rate of 1 Å/sec. As a green dopant, C545T was used. After the deposition of Alq_3, LiF and Al were subsequently deposited at another chamber without breaking the vacuum. During device fabrication, the pressure of the vacuum chamber was kept at $\sim 2\times10^{-6}$ torr. Finally, all devices were encapsulated with BaO in a dry nitrogen glove box under the ambient pressure. The lifetime measurements were carried out at a constant current density of DC 50 mA/cm^2.

3. Results and discussion

Thin films of V_2O_5, pure NPB and doped NPB were fabricated on a quartz glass in a high vacuum chamber by thermal evaporation and the absorption spectra were measured at UV-Vis-NIR range of 200 ~ 2000 nm, as shown in Fig. 1. The formation of charge transfer complex is confirmed by broad band at around 1400 nm. Similar broad absorption bands of the CT complexes have been reported.[4~5] If it is originated from the binding energy of the CT complex, the broad band of 800 ~ 2000 nm should correspond to the energy of 0.6 ~ 1.6 eV which is low enough to be broken easily and generate free holes. V_2O_5 can accept electrons from NPB to form CT complex ($V_2O_5^-$:NPB^+).

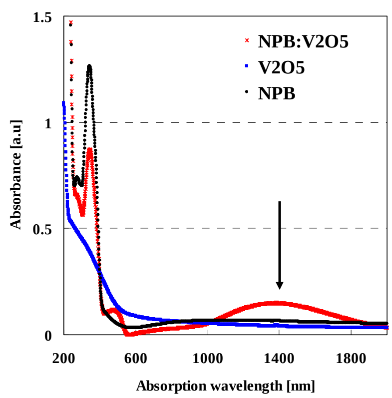

Fig. 1. Absorption spectra of V_2O_5, NPB and V_2O_5 doped NPB films on quartz. (thickness: 150 nm)

To verify p-doping effects of V_2O_5 in NPB, hole-only devices of ITO/pure NPB or V_2O_5 doped NPB (1000 Å)/Al were fabricated. As shown in Fig. 2, a dramatic increase of the hole current can be observed when V_2O_5 is doped into NPB layer. It may be attributed to the decrease of the injection barrier and transfer activation energy to indicate that V_2O_5 acts as an effective p-dopant in NPB film by the formation of the CT complex between V_2O_5 and NPB.

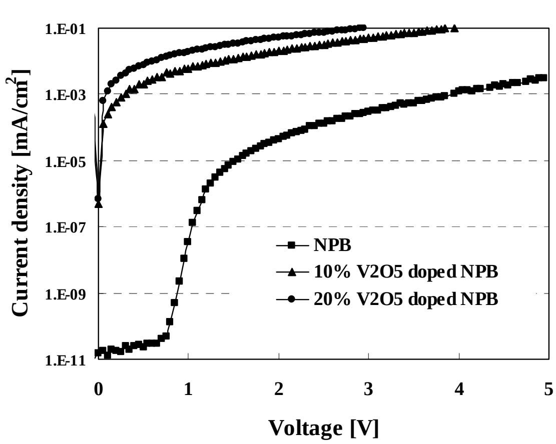

Fig. 2. J-V characteristics of 1000 Å NPB films with various V_2O_5 doping concentrations.

Based on these results, we introduced the V_2O_5 doped NPB layer to common green OLEDs for more quantitative analysis of doping effects on performance of real devices. The doped layer thickness was varied from 25 Å to 500 Å for each V_2O_5 doping concentrations to study both effects on interface and bulk properties whereas the total thickness of HTL from ITO to emission layer was fixed at 700 Å by insertion of pure NPB interlayer. This interlayer prevents exitons from quenching by blocking the diffusion of dopant itself into emission layer and by avoiding hole accumulation at the interface of the EML which can also quench the exitons by formation of exiplex.[6] The structure of resulting devices is as follows.

ITO/V_2O_5 doped NPB(x Å)/NPB(700-x Å)/5 %-C545T doped Alq_3(300 Å)/Alq_3(400 Å)/LiF(10 Å)/Al(800 Å)

Figure 3 shows the current density-voltage(a) and the luminance-current density(b) characteristics of the OLEDs with various thickness of 5 % V_2O_5 doped NPB layer. The control device has 700 Å of un-doped pure NPB as HTL. The current density is significantly enhanced by increasing the thickness of the doped NPB layer whereas slightly lowered quantum efficiencies are shown due to the unbalanced charge effect. The operating voltage at constant current density of 100 mA/cm^2 is 8.0 V for the devices with 5 % V_2O_5 doped layer of which thickness is 500 Å. It is 2.1 V lower than that of the control device.

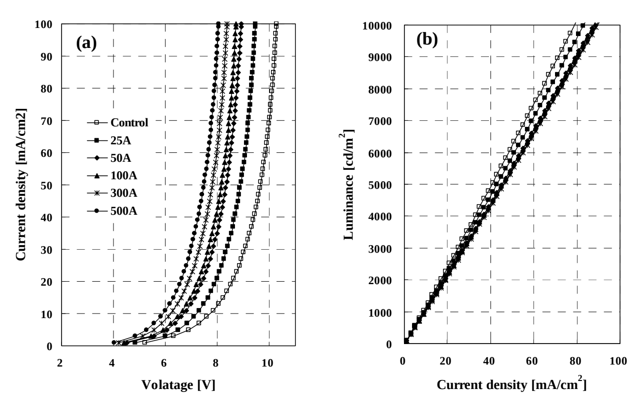

Fig. 3. (a) J-V and (b) L-J plots of OLEDs with various thicknesses of 5 % V_2O_5 doped NPB layer.

Figure 4 is a plot of operation voltages of the devices with various thicknesses of doped layers (0 Å for the control device) at 100 mA/cm^2 of which concentration is 2 %, 5 % and 20 %. The operating voltage is more strongly dependent on the existence of

V_2O_5 doped NPB layer than doping concentration for this range of concentration.

There are two different tendencies of operating voltage reduction for each doping concentrations. First, as increasing the doping thickness up to 100 Å, operating voltage is abruptly dropped and then, further increase of the doped layer thickness up-to 500 Å leads a slow linear drop of the operating voltage. If the straight line is extended to 0 Å thickness of the doped layer and the voltage is named as V_0, the bulk and interface contribution of the voltage reduction can be separated independently. The results obtained by this method are summarized in table 1.

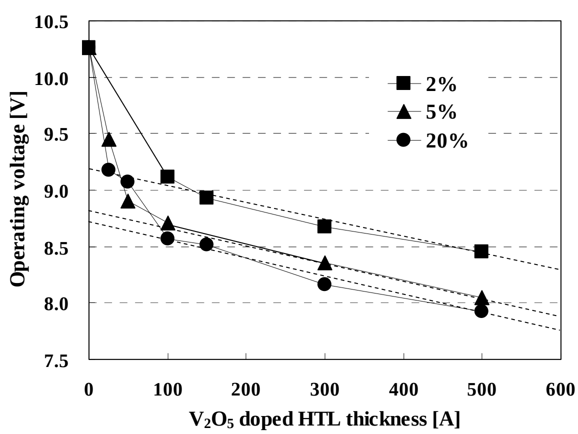

Fig. 4. The plot of operating voltage at constant current density 100 mA/cm^2 for OLEDs with 2 %, 5 % and 20 % V_2O_5 doped NPB layer.

TABLE 1. Operating voltage (100 mA/cm^2) and voltage reduction for each concentration of V_2O_5.

(Control device: 10.1 V)	2 %	5 %	20 %
Operating vol. (500 Å)	8.4	8.0	7.8
V_0	9.2	8.9	8.8
Total voltage reduction	-1.7	-2.1	-2.3
Bulk contribution	-0.8	-0.9	-1.0
Interface contribution	-0.9	-1.2	-1.3

The slow linear drop of the operation voltage may be explained by the reduced bulk resistance of NPB layer because electrical doping was found out to reduce the hoping activation energy. On the other hand, there may be more complicate mechanisms of the predominant drop of operating voltage within 100 Å of the doped layer. Because the carrier injection can be affected by the interface dipole, this interface dipole can be modulated by CT complexes formed by doping and also band bending can come into being which is generally assumed to be absent for pure NPB because of negligible intrinsic carrier density of organic materials. Although it can not be said here that which is dominant mechanism and so more detailed study about interface is needed, it is clear that this interface effect is a more dominant factor of the operating voltage reduction and that this doped layer thickness is needed to be over 100 Å from ITO to achieve sufficient reduction of operating voltage of OLEDs.

In addition to voltage reduction, improved stability of devices with V_2O_5 doped NPB layer was observed. Figure 5 shows the results of the life-time measurement of devices with different thicknesses of 5 % V_2O_5 doped layer. All devices were driven at a fixed current density of 50 mA/cm^2 and the life-time of control device with 700 Å thick NPB layer as HTL was also estimated for comparison. The V_2O_5 doped layer enhances the stability of devices as shown in Fig. 5. For 5 % doping concentration, the half life-time may be over than 800 hrs for 500 Å doping layer thicknesses which is beyond the twice of 350 hrs for control device.

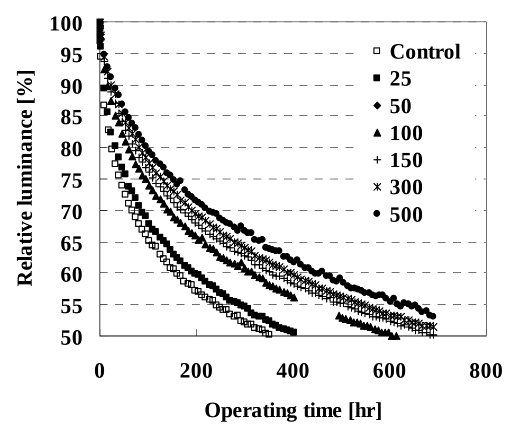

Fig. 5. Results of life-time measurements of OLEDs with pure and 5% V_2O_5 doped NPB layers as HTL.

Generally, the charge balance is one of the most critical factors determining the stability of OLEDs, however this improved stability can not be explained by the charge balance mechanism since we broke down the hole-electron charge balance by increasing the excess hole current of control device by doping. It can be explained by the charge injection and transport mechanisms.

In Fig. 6, the time in which the luminance is 60 % of initial value, is plotted with the doping thickness as variables. By doping V_2O_5 only to 100 Å thick NPB layer, the life-time can be enhanced over than twice of control device showing sharp increment whose tendency is similar to the abrupt voltage reduction as shown before. And then, a more increment of doped layer thickness results to linearly improved half-life time with a gentle slope and this result is also in good agreement with the tendency of voltage reduction at the range of thickness over 100 Å. The improved stability of devices with doped HTL may be attributable to the operating voltage down leading to weak Joule heating effect. This result of life-time measurements strongly suggests that the interface between ITO and NPB plays a more critical role in determining the device stability rather than bulk region of transfer layer.

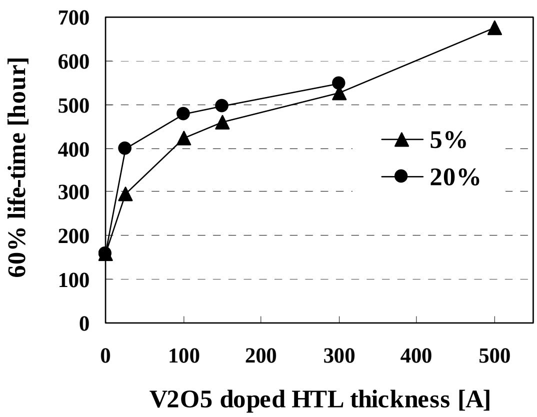

Fig. 6. The 60 % life-time is plotted with variables of doping layer thickness for 5 % and 20 % doping concentration.

4. Summary

We confirmed that V_2O_5 acts as an efficient p-dopant in NPB by formation of CT complex via the study of optical and electrical characteristics of V_2O_5 doped NPB layer. Using the doped layer, reduced operational voltage and improved stability of OLEDs were achieved. Moreover, this voltage reduction can be separated to bulk and interface contribution and the latter is a more dominant factor determining both operation voltage and stability of OLEDs.

Acknowledgment

This study was supported by Mobile Display Center in Samsung SDI.

5. References

1. J. Blochwitz, M. Pfeiffer, T. Fritz, and K. Leo, *Appl. Phys. Lett*. **73**, 729 (1998).
2. D. B. Romero, M. Schaer, L. Zuppiroli, B. Cesar, and B. Francois, *Appl. Phys. Lett*. **67**, 1659 (1995).
3. C. Ganzorig and M. Fujihira, *Appl. Phys. Lett*. **77**, 4211 (2000).
4. J. Endo, T. Matsumoto and J. Kido, *Jpn. J. Appl. Phys.*, **41**, 358 (2002).
5. C. Ganzorig and M. Fujihira, *Appl. Phys. Lett.*, **77**, 4211 (2000).
6. G. He, M. Pfeiffer and K. Leo, *Appl. Phys. Lett.*, **85**, 3911 (2004).