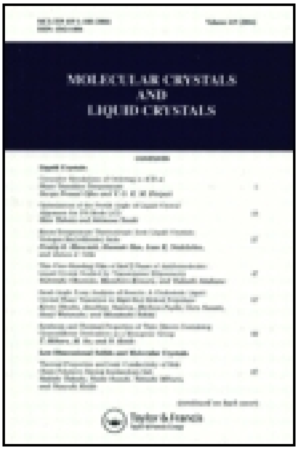

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Enhancement of the Hole Injection and Hole Transport in Organic Light Emitting Devices Utilizing a 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-quinodimethane Doped Hole Transport Layer

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While the current densities of hole only devices with a 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F_4-TCNQ) doped N,N′-bis-(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) hole transport layer (HTL) slightly changed with increasing F_4-TCNQ doping concentration, those of hole only devices with a F_4-TCNQ doped 4,4′,4″-tris(N-(2-naphthyl)-Nphenylamino)triphenylamine (2-TNATA) HTL significantly increased. The hole injection and hole transport of hole only devices were enhanced by inserting an ultra thin F_4-TCNQ layer between an indium-tin-oxide layer and a NPB HTL or a 2-TNATA HTL, regardless of the HTL materials. These results indicate that the hole injection and hole transport in OLEDs utilizing a F_4-TCNQ doped HTL or a F_4-TCNQ thin layer is enhanced.

Keywords: hole transport layer; impurity doping; organic light-emitting devices

I. INTRODUCTION

Organic light-emitting devices (OLEDs) have attracted considerable attention because of their potential applications in promising next-generation full-color flat-panel displays [1–5]. OLED displays have been particularly interesting due to their promising applications,

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which offer many unique advantages of low operating voltage, low power consumption, high contrast, wide viewing angle, and fast response [6,7]. Moderate controls of carrier injection and transport for efficient carrier recombination and more balance of the electrons and the holes are very important for fabricating highly-efficient OLEDs. Potential applications of highly-efficient OLEDs have driven extensive efforts to fabricate various types of OLED devices [8–12]. Among the various methods for improving the performance of carrier injection and carrier transport for highly-efficient OLEDs, an increase in the work function of the indium-tin oxide (ITO) electrode due to surface treatment of the ITO layer is necessary for enhancing device efficiency [10,13]. The insertion of the ultra thin materials, which are copper phthalocyanine, 4,4′,4″-tris(3-methylphenylphenylamino)-triphenylamine (m-MTDATA), 4,4′,4″-tris(N-(2-naphthyl)-Nphenyl-amino)-triphenylamine (2-TNATA), buckminsterfullerene (C_{60}), between the ITO and hole transport layer (HTL) was introduced to enhance the efficiency [14–17]. The HTL doped with p-type 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F_4-TCNQ) impurities significantly improved the efficiency of OLEDs resulting from enhancement of the hole injection and hole transport of OLEDs [18–20]. The F_4-TCNQ impurity acting as a strong electron acceptor plays an important role in the hole transport in the HTL. Even though some works on the enhancement of hole injection and hole transport in the HTL due to the p-type impurity doping have been performed, systematic studies concerning the enhancement of the carrier injection and transport in OLEDs utilizing an impurity doped HTL are necessary for achieving highly-efficient OLEDs.

This paper reports data for enhancement of the hole injection and hole transport in OLEDs fabricated utilizing a F_4-TCNQ doped N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′biphenyl 4,4′-diamine (NPB) HTL or a F_4-TCNQ doped 2-TNATA HTL grown by using organic molecular-beam deposition (OMBD). Current density-voltage measurements were carried out to investigate the electrical properties of the hole only devices. Carrier injection and transport mechanisms for more balance of the electrons and the holes in the OLEDs are described on the basis of the experimental results.

II. EXPERIMENT DETAILS

The sheet resistivity of the ITO thin films coated on glass substrates used in this study was 15 Ω/square. The ITO substrates were cleaned by using acetone and methanol at 60°C for 5 min and were rinsed in de-ionized water thoroughly. After the chemically cleaned ITO

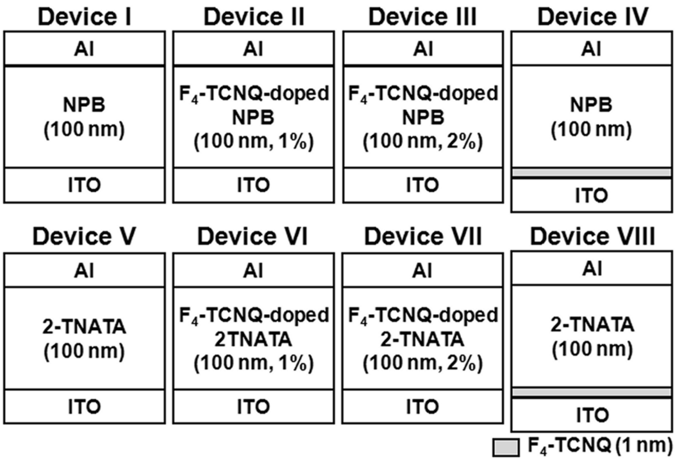

FIGURE 1 Schematic diagrams of the hole only devices used in this work.

substrates were then dried by using N_2 gas with a purity of 99.9999%, the substrates were treated with oxygen plasma for 10 min. The eight kinds of samples used in this study were deposited on the ITO thin films coated on glass substrates by using OMBD with effusion cells and shutters. The schematic diagrams of the samples fabricated in this study are shown in Figure 1. The electron injection into the organic layers is interrupted in the all hole only devices. The NPB layers of devices I, II, III, and IV and the 2-TNATA layers of devices V, VI, VII, and VIII act as HTLs in OLEDs. The doping concentration of the F_4-TCNQ embedded in the HTLs for devices II and VI is 1 vol.%, and that for devices III and VII is 2 vol.%. An ultra thin F_4-TCNQ layer inserted between the ITO anode and the NPB layer for device IV or between the ITO anode and the 2-TNATA layer for device VIII. The evaporation rate of the host and the dopant materials can be controlled independently by using two separate quartz thickness monitors, which adjust the doping concentration. The depositions of the OLED layers were done at a substrate temperature of 27°C and at a system pressure of 5×10^{-6} Torr. The growth rates of the organic layers, the doping impurities and the metal layers are approximately 0.1, 0.01, and 0.5 Å/s, respectively. The emitting area is $5 \times 5\,mm^2$.

III. RESULTS AND DISCUSSION

Figure 2 shows the current densities as functions of the applied voltage characteristics for hole only devices with various F_4-TCNQ doping

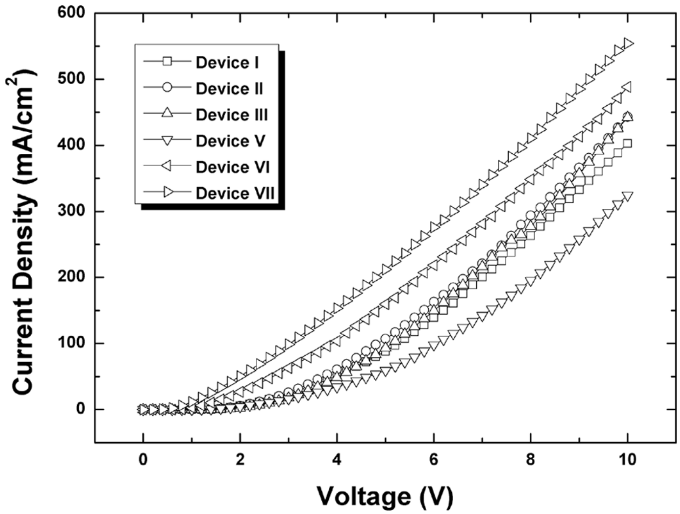

FIGURE 2 Current densities as functions of the applied voltage characteristics of devices I, II, III, V, VI, and VII.

concentrations. Because the highest occupied molecular orbital (HOMO) levels of the NPB and the 2-TNATA are 5.4 and 5.1 eV, respectively, the hole injection barrier of device I with an undoped NPB HTL is larger than the corresponding barrier of device V with a 2-TNATA HTL. However, because the hole mobility of the NPB HTL is higher that of the 2-TNATA HTL, the current density of device I at the same operating voltage is larger than that of device V. The current densities as functions of the applied voltage for hole only devices with a NPB HTL or a 2-TNATA HTL show different trends dependent on the F_4-TCNQ doping concentration. While the current densities as functions of applied voltage curves for devices I, II, and III with a F_4-TCNQ-doped NPB HTL show almost similar characteristics, regardless of the magnitude of the F_4-TCNQ doping concentration, the corresponding current densities for devices V, VI, and VII with a F_4-TCNQ-doped 2-TNATA HTL increase with an increase in the doping concentration of F_4-TCNQ. The current density of device VII with a 2 vol.% doping concentration at the same operating voltage shows the largest among the samples. Because the lowest unoccupied molecular orbital (LUMO) level of the F_4-TCNQ dopant and the HOMO level of the NPB HTL or the 2-TNATA HTL are almost same, the electrons existing in the HOMO level of the NPB HTL or the 2-TNATA HTL are transferred into the LUMO of the F_4-TCNQ dopant existing in the HTL [19,20].

The hole concentration in the NPB HTL or the 2-TNATA HTL increases due to the electron transfer from the HOMO level of the NPB HTL or the 2-TNATA HTL to the LUMO level of the F_4-TCNQ dopant, resulting in an improvement in the conductivity of the F_4-TCNQ doped HTL. However, the current densities of the devices with a NPB HTL are not significantly improved because the maximum doping concentration of the F_4-TCNQ dopant in the NPB HTL becomes saturated due to the limited sticking coefficient of the F_4-TCNQ dopant [20].

Figure 3 shows the current densities as functions of the applied voltage characteristics of devices I, IV, V and VIII without and with an 1-nm ultra thin F_4-TCNQ layer embedded between the ITO anode and the HTL. The operating voltages of devices IV and VIII with an ultra thin F_4-TCNQ layer are smaller than those of devices I and V without an F_4-TCNQ layer. The decrease in the operating voltage for devices IV and VIII with an ultra thin F_4-TCNQ layer is attributed to the chemical potential shift due to the existence of the interfacial dipole [21]. The interfacial dipole layer existing between the ITO anode and the NPB layer or the 2-TNATA layer decreases the magnitude of the carrier injection barrier between the electrode and the organic layer. The F_4-TCNQ organic material acting as a strong electron acceptor is typically used as an interfacial dipole layer. The ultra thin F_4-TCNQ layer forms the interfacial dipole at the heterointerface between the ITO anode and the NPB HTL or the 2-TNATA HTL, and

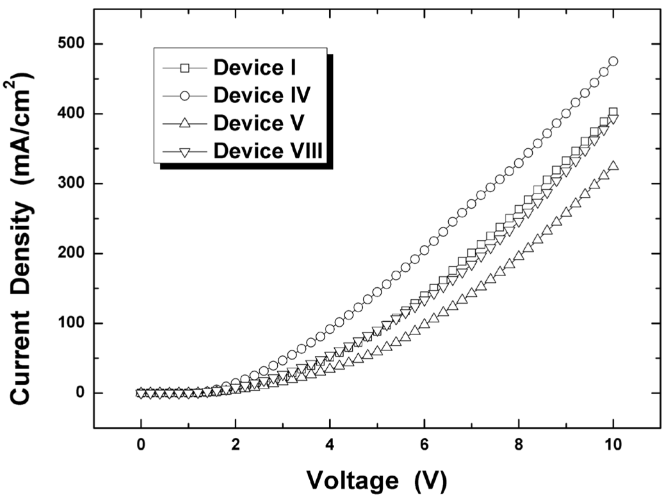

FIGURE 3 Current densities as functions of the applied voltage characteristics of devices I, IV, V, and VIII.

the dipole layer decreases the magnitude of the hole injection barrier. A decrease in the operating voltage of the OLEDs might be significantly affected due to the HTL materials because the magnitude in the decrease of the operating voltages for devices IV and VIII is almost same.

IV. SUMMARY AND CONCLUSION

The electrical properties of hole only devices with a NPB HTL or a 2-TNATA HTL doped with a F_4-TCNQ were investigated. While the hole injection of the hole only device with an ultra thin F_4-TCNQ layer between the ITO anode and the NPB HTL or the 2-TNATA HTL was significantly enhanced, that of hole only device with a F_4-TCNQ-doped NPB HTL was slightly improved. While the hole transport of the hole only devices with a F_4-TCNQ-doped 2-TNATA HTL was enhanced due to an increase in the doping concentration, that of the hole only devices with a F_4-TCNQ-doped NPB HTL was not significantly improved because the maximum doping concentration of the F_4-TCNQ dopant in the NPB HTL became saturated due to the limited sticking coefficient of the F_4-TCNQ dopant. These results indicate that the hole injection and hole transport of OLEDs can be improved by utilizing an ultra thin F_4-TCNQ layer between the ITO anode and the NPB HTL or the 2-TNATA HTL. Furthermore, the present observations can help improve understanding of the enhancement of the carrier injection and carrier transport in OLEDs utilizing a F_4-TCNQ-doped HTL.

REFERENCES

[1] Tang, C. W. & Vanslyke, S. A. (1987). *Appl. Phys. Lett.*, *51*, 913.

[2] Parthasarathy, G., Adachi, C., Burrows, P. E., & Forrest, S. R. (2002). *Appl. Phys. Lett.*, *76*, 2128.

[3] Kim, Y., Oh, E., Lim, H., & Ha, C.-S. (2006). *Appl. Phys. Lett.*, *88*, 043504.

[4] Liao, L. S., Klubek, K. P., & Tang, C. W. (2004). *Appl. Phys. Lett.*, *84*, 167.

[5] Mazzeo, M., Vitale, V., Sala, F. D., Anni, M., Barbarella, G., Favaretto, L., Sotgiu, G., Cingolani, R., & Gigli, G. (2005). *Adv. Mater.*, *17*, 34.

[6] Hung, L. S. & Chen, C. H. (2002). *Mater. Sci. Eng., R, 39*, 143.

[7] Xie, Z. Y. & Hung, L. S. (2004). *Appl. Phys. Lett.*, *84*, 1207.

[8] Shiga, T., Fujikawa, H., & Taga, Y. (2003). *J. Appl. Phys.*, *93*, 19.

[9] Chen, C.-W., Lin, C.-L., & Wu, C.-C. (2004). *Appl. Phys. Lett.*, *85*, 2469.

[10] Kim, J. S., Granstrom, M., Friend, R. H., Johansson, N., Salaneck, W. R., Daik, R., Feast, W. J., & Cacialli, F. (1998). *J. Appl. Phys.*, *84*, 6859.

[11] Yoon, Y. B., Yang, H. W., Choo, D. C., Kim, T. W., & Oh, H. S. (2005). *Solid State Communications*, *134*, 367.

[12] Choo, D. C., Yoon, Y. B., Lee, D. U., Kim, T. W., Lee, H. K., & Kim, Y. K. (2007). *Mol. Cryst. Liq. Cryst.*, *470*, 269.

[13] Mason, M. G., Hung, L. S., Tang, C. W., Lee, S. T., Wong, K. W., & Wang, M. (1999). *J. Appl. Phys.*, *86*, 1688.
[14] VanSlyke, S. A., Chen, C. H., & Tang, C. W. (1996). *Appl. Phys. Lett.*, *69*, 2160.
[15] Shirota, Y., Kuwabara, Y., Inada, H., Wakimoto, T., Nakada, H., Yonemoto, Y., Kawami, S., & Imai, K. (1994). *Appl. Phys. Lett.*, *65*, 807.
[16] Shirota, Y., Kuwabara, Y., Okuda, D., Ogawa, H., Inada, H., Wakimoto, T., Nakada, H., Yonemoto, Y., Kawami, S., & Imai, K. (1997). *J. Luminescence 72–74*, 985.
[17] Hong, I. H., Lee, M. W., Koo, Y. M., Jeong, H., Kim, T. S., & Song, O. K. (2005). *Appl. Phys. Lett.*, *87*, 063502.
[18] Pfeiffer, M., Leo, K., Zhou, X., Huang, J. S., Hofmann, M., Werner, A., & Blochwitz, J. (2003). *Org. Electron.*, *4*, 89.
[19] Zhou, X., Blochwitz, J., Pfeiffer, M., Nollau, A., Fritz, T., & Leo, K. (2001). *Adv. Funct. Mater.*, *11*, 310.
[20] Gao, W. & Kahn, A. (2003). *J. Appl. Phys.*, *94*, 359.
[21] Nüesch, F., Rotzinger, F., Si-Ahmed, L., & Zuppiroli, L. (1998). *Chem. Phys. Lett.*, *288*, 861.