Solution-processed Small Organic Electrophosphorescent Devices with Arylamine Polymer Buffer Layer

Katsutoshi Hirano[†], Shigeki Naka^{†,a}, Hiroyuki Okada[†], Hiroyoshi Onnagawa[†],
Toshimitsu Nakai[‡], and Hideki Sato[‡]

[†]*Faculty of Engineering, University of Toyama, Toyama 930-8555, Japan*

[‡]*Mitsubishi Chemical Group, Science and Technology Research Center, Inc.,
Yokohama 227-8502, Japan
nak@eng.u-toyama.ac.jp*

Solution-processed organic electrophosphorescent devices with arylamine polymer buffer layer have been investigated. Device characteristics were similar to the device using commonly used conducting polymer as buffer layer, and the uniform emission was obtained in the device. The lifetime of the device, defined as half-luminous at an initial luminance of 1,000 cd/m², was 40 h.

Keywords: arylamine polymer, solution-process, small organic molecules

1. Introduction

Organic light-emitting diodes (OLEDs) have excellent properties of low driving voltage and bright emission.[1,2] One of the interesting research topics is the investigation of organic electrophosphorescent OLEDs (PHOLEDs).[3-6] The PHOLED exhibits an ultimate quantum efficiency of 100 % [5] and power efficiencies of around 70 lm/W [6]. On the other hand, the fabrication of solution-processed OLEDs (SP-OLEDs) is simple [7-11] and is promising for patterning an organic layer using an ink-jet printing (IJP) technique [12,13]. For solution-processed OLEDs with small organic molecules, a device with equivalent performance and reliability to those of evaporation-processed OLEDs could be realized.

In order to improve reliability, a buffer layer such as a conducting polymer is used for obtaining a flat surface. In this paper, we describe the performance of solution-processed small organic PHOLED with arylamine polymer buffer layer [14].

2. Experiment

A p-doped arylamine polymer (MCC-PC1020; Mitsubishi Chemical) and poly(ethylene dioxythiophene)/poly(styrene sulfonate) (PEDOT;

H. C. Starck-VTECH) as a hole injection buffer materials, bis[*N*-(1-naphthyl)-*N*-phenyl] benzidine (α -NPD; Dojindo Lab.) as hole transport material, 4,4'-*N,N*-dicarbazole-biphenyl (CBP; Dojindo Lab.) as a host material, *fac*-tris(2-(*p*-tolyl)-pyridine) iridium (Ir(tpy)₃; American Dye Source) as a phosphorescent material, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP; Kanto Kagaku) as an electron transport material were used in this study.

Indium zinc oxide [15] (IZO) coated glass substrate purchased from Kuramoto Seisakusho was patterned using conventional photolithography for anode. The etchant used was oxalic acid (HOCCOOH, 2.5 %, 32°C). A cross sectional view of the SEM observation reveals that the taper angle and roughness at the IZO edge were smaller than that those at the ITO edge [15, 16].

Thickness of MCC-PC1020 spin-coated film was 50 nm. On the other hand, thickness of PEDOT film was 50 nm, and subsequently the sample was dried in air at 200°C for 1 h. Next, the emission layer was also spin-coated from chloroform solution and subsequently dried in vacuum at 60°C for 10 h. MCC-PC1020 and PEDOT films do not dissolve at the spin-coating process of emission layer. Then a 20 nm BCP layer

was evaporated from a molybdenum boat. Finally, a bilayer cathode of LiF (1 nm)/Al (70 nm) was evaporated sequentially from a tungsten basket or boat without breaking vacuum. The evaporation rate and thickness of the evaporated films were monitored with a quartz oscillator. The glass substrate was kept at room temperature during evaporation. Finally, the devices were encapsulated using the glass substrate and epoxy resin in a nitrogen atmosphere using a glove bag. The device area was $2 \times 2 \text{ mm}^2$.

The current and luminance versus applied voltage characteristics were measured using a semiconductor parameter analyzer (HP 4145A) connected with a luminance meter (Topcon BM-3). The time-dependent luminance and voltage in the constant-current mode were measured using hand-made current-control circuits, a data logger (OMRON K8DL) and a computer controlled system.

3. Results and Discussion

First, a comparison with the buffer layers was tested for the device ITO/ MCC-PC1020 or PEDOT/ α -NPD+CBP+Ir(tpy)₃ (80 nm)/ BCP/ LiF/ Al structure. Figure 1 show current density (J)-applied voltage (V) and luminance (L)-current density (J) characteristics of the device. In the MCC-PC1020 device, the J - V characteristics shifted to low operational voltage in high current region. The luminances at $J=100 \text{ mA/cm}^2$ were 16,400 and 16,300 cd/m^2 for MCC-PC1020 and PEDOT devices, respectively. A maximum EL efficiency of 16.9 lm/W ($J=0.29 \text{ mA/cm}^2$) was obtained for the MCC-PC1020 device. Figure 2 shows microscopic observations of the emission. Uniform emission was obtained in MCC-PC1020 device. On the other hand, a local bright emission was obtained at the IZO edge and the periphery of the device area in the PEDOT device. A step coverage of the organic layer at the IZO edge a largely influence on uniformity because current is concentrated at the thin organic layer. Figure 3 shows result of durability tests under constant current density at initial luminance of $L_0=1,000 \text{ cd/m}^2$. The initial current densities of the device with MCC-PC1020 and with PEDOT were 3.63 and 4.30 mA/cm^2 , respectively. These characteristics can be fitted in the Weibull distribution as

$$L = L_0 \exp \left\{ - \left(\frac{t}{\eta} \right)^m \right\},$$

where, L_0 is the initial luminance and t is the time.[17] Parameter η is the scale parameter with dimension of time. And m is the shape parameter depends on curvature of the characteristics. The half-life of MCC-PC1020 and PEDOT devices were 40 h and 33 h, the scale parameters were 73.2 and 48.3 h and the shape parameters were 0.59 and 0.61, respectively. Solid lines show approximation curves using the Weibull distribution. The shap

Fig. 1 J - V and L - J characteristics varied with buffer layer.

Fig. 2 Microscopic image of emission pattern.

Fig. 3 Long-term durability varied with buffer layer.

parameter of MCC-PC1020 device was identical to that of PEDOT device. Therefore, degradation mechanism of these devices will be equivalent.

Figure 4 show J - V and L - J characteristics with varied thickness of emission layer for

MCC-PC1020 device. The device structure is ITO/MCC-PC1020/ α -NPD+CBP+Ir(tpy)₃ (100 nm)/BCP/ LiF/ Al. The J - V characteristics shifted to high operational voltage with increasing thickness of emission layer. In addition, the luminance was also increased and saturated at the thickness of over 80 nm. Figure 5 shows the result of durability tests with varied thickness of emission layer under the constant-current mode at the initial luminance of 1,000 cd/m². The constant current densities of the device with thickness of emission layer of 40, 60, 80, and 100 nm were 19.3, 11.0, 3.63, and 4.73 mA/cm², respectively. The half-life of the devices with thickness of emission layer of 40, 60, 80, and

Fig. 4 J - V and L - J characteristics varied with emission layer thickness.

100 nm were 2, 15, 40, and 40 h, respectively. The scale parameters were 6.6, 40.7, 73.2 and 60.3 h and the shape parameters were 0.43, 0.40, 0.59 and 0.80, respectively. In this case, the shape parameters between all conditions were different. This may due to the difference degradation mode with varied acceleration condition. In either case, these characteristics can be fitted using the Weibull function.

4. Conclusion

Solution-processed small organic electro-phosphorescent devices with arylamine polymer buffer layer had been investigated. The operational voltage in MCC-PC1020 device was lower than PEDOT device. The lifetime of the device, defined as half-luminous at an initial luminance of 1,000 cd/m^2 , was 40 h. The improvement of lifetime will be expected, particularly in the optimizations of the device structure, such as introducing a stable electron transport layer, optimizing dopant concentration, and achieving a flat electrode surface without particles and a smoother electrode edge.

References

1. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51** (1987) 913.
2. T. Tsutsui, *MRS Bull.* **22** (1997) 39.
3. M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature* **395** (1998) 151.
4. M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **75** (1999) 4.
5. C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *J. Appl. Phys.* **90** (2001) 5048.
6. M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, and Y. Taga, *Appl. Phys. Lett.* **79** (2001) 156.
7. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holms, *Nature* **347** (1990) 539.
8. Y. Mori, H. Endo, and Y. Hayashi, *Oyo Buturi* **61** (1992) 1044 [in Japanese].
9. J. Kido, H. Shionoya and K. Nagai, *Appl. Phys. Lett.* **67** (1995) 2281.
10. J. K. Borchardt, *Mater. Today* **9** (2004) 42.
11. S.-C. Lo, N. A. H. Male, J. P. J. Markham, S. W. Magennis, P. L. Burn, O. V. Salata, and I. D. Samuel, *Adv. Mater.* **14** (2002) 975.
12. T. Shimoda, S. Kanbe, H. Kobayashi, S. Seki, H. Kiguchi, I. Yudasaka, M. Kimura, and S. Miyashita, *SID 99 Dig.* (1999) 376.
13. R. Satoh, S. Naka, M. Shibata, H. Okada, H. Onnagawa, T. Miyabayashi, and T. Inoue, *Jpn. J. Appl. Phys.* **43** (2004) 7725.
14. S. Watanabe, Y. Agata, D. Tanaka, and J. Kido, *J. Photopolym. Sci. Technol.* **18** (2005) 83.
15. K. Inoue, *Monthly Display* **4** (1998) 15 [in Japanese].
16. M. Ooe, S. Naka, H. Okada, and H. Onnagawa, *Jpn. J. Appl. Phys.* **45** (2006) 250.
17. Y. Motono, S. Naka, H. Okada, and H. Onnagawa, *Proc. IDW/AD'05* (2005) 769.

Fig. 5 Long-term durability test varied with emission layer thickness.