An effective cathode structure for inverted top-emitting organic light-emitting devices

Chieh-Wei Chen, Chun-Liang Lin, and Chung-Chih Wu^{a)}

Department of Electrical Engineering, Graduate Institute of Electro-optical Engineering, and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China

(Received 29 April 2004; accepted 29 July 2004)

Inverted top-emitting organic light-emitting devices (OLEDs) combine technical merits of top-emitting OLEDs and inverted OLEDs for active-matrix OLED displays. One major challenge in inverted top-emitting OLEDs, however, is to prepare a reflective bottom cathode capable of effective electron injection. In this letter, we report an effective cathode structure for enhancing the electron-injection capability of the bottom cathode in inverted top-emitting OLEDs. Such an approach does not involve handling reactive metals during fabrication and permits use of highly reflective materials such as Al and Ag as the bottom cathodes. Efficient inverted top-emitting devices employing such a cathode scheme have been demonstrated. © 2004 American Institute of Physics. [DOI: 10.1063/1.1798392]

Active-matrix architectures have been widely adopted in high-performance displays using organic light-emitting devices (OLEDs).¹ Active-matrix OLED displays (AMOLEDs) in general will benefit from adopting top-emitting OLED structures, which remove limitations in the optical transparency of substrates and on the OLED filling factor of pixels.^{2–5} Inverting top-emitting OLEDs, i.e., making OLEDs that have a reflective cathode at bottom and a (semi-) transparent anode on top, would render feasible use of generally superior *n*-type transistors rather than *p*-type transistors in the AMOLED pixel circuitry and further enhance performance.^{6–9} One major challenge in inverted top-emitting OLEDs, however, is to prepare a reflective bottom cathode providing effective electron injection. In a few reported inverted OLEDs,^{6–9} the preparation of electron-injecting bottom cathodes all involves handling highly reactive low-work-function metals during fabrication. In one way, they were deposited as the cathode layer directly.^{6,8} However, changing the formation process of the contact leads to the degraded electron-injecting capability. Furthermore, it is not practical for actual display fabrication. In another way, reactive metals were co-deposited with organic electron-transport materials to form an *n*-doped layer for facilitating electron injection from the bottom cathode.^{7,9} Yet, there remain issues in diffusion of metal dopants and thus operation reliability.^{10,11} In this letter, we report an effective bottom cathode structure for enhancing the electron injection in inverted top-emitting OLEDs. Such a cathode structure does not involve handling reactive metals during fabrication and permits use of highly reflective materials such as Al and Ag as the bottom cathode.

One effective cathode structure often used in conventional OLEDs is to deposit an ultrathin layer (~1 nm) of alkali or alkaline earth metal complex (e.g., LiF) between the metal cathode and the organic electron-transport layer [e.g., tris-(8-hydroxyquinoline) aluminum, Alq₃].^{12,13} Previous studies have revealed that in such configurations the forma-

tion of an effective cathode with the relatively high-work-function metal is attributed to the release of the alkali or alkaline earth metal from the metal complex in depositing the metal cathode and subsequent reactions to form anions of the electron-transport material.^{14–16} In the case of Alq₃/LiF/Al, such thermodynamically allowed reaction can be expressed as $3 \text{LiF} + \text{Al} + 3 \text{Alq}_3 \rightarrow \text{AlF}_3 + 3 \text{Li}^+ \text{Alq}_3^-$.^{14–16} Such reactions result in enhanced electron injection due to formation of a thin *n*-doped Alq₃ layer as in the cases of using Li-doped Alq₃ as the electron-injection layer or using Li as the low-work-function cathode.^{17,18} It is also shown that an ultrathin Al overcoat (~1 nm) on LiF on Alq₃ is sufficient to induce such a reaction, and that the reacted layer has a shallow nature of only 1 nm or less.^{14,15} It is therefore possible to employ the ultrathin Alq₃/LiF/Al trilayer as a composite electron-injection layer between various organic electron-transport layers and conductive cathode layers in conventional OLED structures (with the cathode on top), as demonstrated in a few cases.^{4,14,19} Whether such an electron-injection scheme may be applied to bottom cathodes of inverted top-emitting OLEDs is the subject of this study.

To evaluate the effect of the ultrathin Alq₃/LiF/Al trilayer on electron injection from the bottom cathode, symmetrical “double-cathode” devices with the structure of substrate/bottom cathode (Ag or Al, 80 nm)/ultrathin Alq₃-LiF-Al trilayer/Alq₃ (80 nm)/LiF (0.5 nm)/Al (100 nm) were fabricated and tested. The composite trilayer on top of the bottom cathode in sequence consists of 0.2 nm Alq₃, 0.2 nm LiF, and 0.3 nm Al. For comparison, control devices with nearly the same configuration but without the ultrathin trilayer were also fabricated. In these devices, the top Al electrode with the thin LiF injection layer serves as the “benchmark” cathode scheme for comparison with the bottom cathodes examined. Bottom Al or Ag serves as the electron-injecting electrode when biased negatively, and as a counterelectrode when biased conversely.

Figures 1(a) and 1(b) show the current–voltage characteristics of the double-cathode devices with Ag and Al bottom cathodes, respectively. Without the ultrathin Alq₃-LiF-Al trilayer, the *I*–*V* characteristics are somewhat

^{a)} Author to whom correspondence should be addressed; electronic mail: chungwu@cc.ee.ntu.edu.tw

FIG. 1. I - V characteristics of double-cathode devices: (a) using Ag as the bottom cathode with and without the ultrathin Alq_3 -LiF-Al electron-injection trilayer, and (b) using Al as the bottom cathode with and without the ultrathin Alq_3 -LiF-Al trilayer.

rectified with the reverse-bias current (injection from the bottom) being lower than the forward-bias current (injection from the top). The differences are over three orders of magnitudes for Ag and over one order of magnitude for Al. With the ultrathin trilayer inserted, the injection current under reverse bias is significantly enhanced for both cases to become nearly symmetrical with that under forward bias, indicating comparably effective electron injection from top and bottom cathodes. These results indicate that the reaction in the ultrathin Alq_3 -LiF-Al trilayer produces a structure or composition that largely facilitates electron injection regardless of the cathode being deposited before or after the formation of this injection layer and regardless of the cathode being Ag or Al. Such features certainly give much greater flexibility in the design of cathode structures and in applications to various device configurations.

To demonstrate the usefulness of the present cathode structures, inverted top-emitting OLEDs with the structure of Fig. 2 were fabricated and characterized. The devices were built on glass substrates precoated with Ag or Al (80 nm), which was used as the cathode directly [Fig. 2(b)] or was covered with the ultrathin Alq_3 -LiF-Al trilayer before following deposition [Fig. 2(a)]. The organic multilayer structure followed sequentially consists of Alq_3 (50 nm) as the electron-transport and emitting layer, α -naphthylphenylbiphenyl diamine (α -NPD, 40 nm and 45 nm for devices using Ag and Al cathodes, respectively) as the hole-transport layer,¹² 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine (m-MTDATA, 20 nm) doped with 2 wt % of tetrafluorotetracyanoquinodimethane (F4-TCNQ) as the hole-injection layer.²⁰ A thin layer (20 nm) of Ag, which has relatively low optical absorption and the highest conductivity among all metals, is deposited as the (semi-)transparent anode with a low sheet resistance of $\sim 1 \Omega/\text{square}$. The hole-injection capability from top Ag into m-MTDATA:F4-TCNQ is examined using the symmetrical "double-anode" device structure of indium-

FIG. 2. Device structures of the inverted top-emitting devices: (a) with and (b) without the ultrathin Alq_3 -LiF-Al trilayer.

FIG. 3. I - V characteristics of the double-anode devices: ITO/m-MTDATA:F4-TCNQ (100 nm)/Ag, and ITO/m-MTDATA (100 nm)/Ag.

tin-oxide (ITO)/m-MTDATA:F4-TCNQ (100 nm)/Ag. Figure 3 shows that the hole-injection current from Ag (reverse bias) is symmetrical with the hole-injection current from the "benchmark" ITO anode (forward bias), confirming the effectiveness of the F4-TCNQ p -doping on facilitating hole injection from Ag into m-MTDATA. Without p -doping, hole injection from Ag into m-MTDATA is over two orders of magnitudes lower than that from ITO (Fig. 3). Indeed we have found that when the ultrathin electron-injection trilayer is used in devices, hole injection from Ag into m-MTDATA (no p -doping) cannot match with electron injection, leading to very low emission efficiency. The Ag anode is further capped with a high-refractive-index dielectric layer of thermally evaporated TeO_2 ($n \sim 2.2$ – 2.3) as an index-matching (or antireflection) layer to enhance the optical transmission of the thin metal anode.^{5,21} The thicknesses of organic layers and the TeO_2 layer (30 nm) had been optimized for colors and efficiencies of devices according to a methodology described in Ref. 21. The devices were fabricated, encapsulated, and characterized as described in Refs. 5 and 21.

Figure 4(a) shows the measured electroluminescence (EL) spectra with relative intensities (symbols) at viewing angles of 0° , 30° , and 60° off the surface normal for the top-emitting device using the Ag cathode with the ultrathin trilayer. EL spectra of devices using the Al cathode (not shown) are similar to those in Fig. 4(a). EL of the top-emitting devices shows more saturated colors in comparison with photoluminescence (PL) of Alq_3 due to the microcavity effect.²¹ The usual variation of colors with viewing angles associated with microcavity effects has been nearly eliminated in the present case through optimizing optical structures of devices (i.e., thicknesses of organic and dielectric layers) according to a methodology developed previously.²¹ Figure 4(a) also shows that the simulated EL spectra (lines) calculated using the electric-dipole-based classical electromagnetic model²¹ are in excellent agreement with measured results (symbols). In the simulation, it is also found that the effects of the ultrathin injection trilayer on optical characteristics are negligible and that the optimal layer thicknesses are slightly different for Al and Ag cathodes due to differences in their optical constants.

Figure 4(b) compares the I - V characteristics of four inverted top-emitting devices examined. As expected, devices with the electron-injection trilayer exhibit lower voltages than devices without the trilayer no matter whether Ag or Al is used as the cathode. Devices using the Al cathode show somewhat higher voltages than devices using the Ag cathode due to thicker organic films used for optimizing optical char-

FIG. 4. (a) Measured (symbols) and calculated (solid lines) EL spectra with relative intensities at viewing angles of 0°, 30°, 60° off the surface normal for the top-emitting device using the Ag bottom cathode with the ultrathin trilayer. PL of Alq₃ is also shown for comparison. (b) I - V characteristics, and (c) L - I characteristics of the four inverted top-emitting devices using the Ag cathode with/without the injection trilayer, and the Al cathode with/without the injection trilayer. Inset of (c): comparison of efficiency characteristics of the four devices.

acteristics. Figure 4(c) and the inset of Fig. 4(c) compare the brightness-current (L - I) characteristics and the efficiency characteristics of the four devices, respectively. Without the electron-injection trilayer, the device using the Al cathode shows a low EL efficiency of 1.7 cd/A and the device using the Ag cathode gives no emission at all. Such results indicate that electron injection from Ag to Alq₃ is extremely unbalanced with hole injection, and that the situation for Al is less worse yet still not competitive with hole injection. With the electron-injection trilayer, the Ag and Al devices achieve efficiencies of 5.3 and 4.5 cd/A, respectively. Both are comparable to or somewhat higher than EL efficiencies of a state-of-the-art nondoped (bottom-emitting) Alq₃ device,^{12,14,17,18} indicating that electron injection has been enhanced to become rather balanced with hole injection.

In summary, we report the use of the ultrathin Alq₃-LiF-Al trilayer as an effective composite electron-injection layer for bottom cathodes of inverted top-emitting OLEDs. Such an approach does not involve handling reactive metals during fabrication and permits use of highly reflective materials such as Al and Ag as the bottom cathodes. Finally, it should be mentioned that although only the case of Alq₃-LiF-Al is examined in this report, such an electron-injection scheme may be generalized to other organic-metal complex-metal systems as long as similar reactions occur.

The authors would like to acknowledge financial support from National Science Council and Industrial Technology Research Institute/Electronics Research and Service Organization (ITRI/ERSO) of the Republic of China. C.-W.C. is also grateful for financial support from the MediaTek Fellowship.

- ¹R. M. A. Dawson and M. G. Kane, 2001 *Society for Information Display (SID) International Symposium*, Digest of Technical Papers (San Jose, CA, 2001), p. 372.
- ²H. Riel, S. Karg, T. Beierlein, B. Ruhstaller, and W. Rieß, *Appl. Phys. Lett.* **82**, 466 (2003).
- ³M.-H. Lu, M. S. Weaver, T. X. Zhou, M. Rothman, R. C. Kwong, M. Hack, and J. J. Brown, *Appl. Phys. Lett.* **81**, 3921 (2002).
- ⁴L. S. Hung, C. W. Tang, M. G. Mason, P. Raychaudhuri, and J. Madathil, *Appl. Phys. Lett.* **78**, 544 (2001).
- ⁵C.-W. Chen, P.-Y. Hsieh, H.-H. Chiang, C.-L. Lin, H.-M. Wu, and C.-C. Wu, *Appl. Phys. Lett.* **83**, 5127 (2003).
- ⁶V. Bulović, P. Tian, P. E. Burrows, M. R. Gokhale, and S. R. Forrest, *Appl. Phys. Lett.* **70**, 2954 (1997).
- ⁷X. Zhou, M. Pfeiffer, J. S. Huang, J. Blochwitz-Nimoth, D. S. Qin, A. Werner, J. Drechsel, B. Maennig, and K. Leo, *Appl. Phys. Lett.* **81**, 922 (2002).
- ⁸T. Dobbertin, M. Kroeger, D. Heithecker, D. Schneider, D. Metzendorf, H. Neuner, E. Becker, H.-H. Johannes, and W. Kowalsky, *Appl. Phys. Lett.* **82**, 284 (2003).
- ⁹T. Dobbertin, O. Werner, J. Meyer, A. Kammoun, D. Schneider, T. Riedl, E. Becker, H.-H. Johannes, and W. Kowalsky, *Appl. Phys. Lett.* **83**, 5071 (2003).
- ¹⁰B. W. D'Andrade, S. R. Forrest, and A. B. Chwang, *Appl. Phys. Lett.* **83**, 3858 (2003).
- ¹¹G. Parthasarathy, C. Shen, A. Kahn, and S. R. Forrest, *J. Appl. Phys.* **89**, 4986 (2001).
- ¹²L. S. Hung, C. W. Tang, and M. G. Mason, *Appl. Phys. Lett.* **70**, 152 (1997).
- ¹³Q. Xu, J. Ouyang, Y. Yang, T. Ito, and J. Kido, *Appl. Phys. Lett.* **83**, 4695 (2003).
- ¹⁴L. S. Hung, R. Q. Zhang, P. He, and G. Mason, *J. Phys. D* **35**, 103 (2002).
- ¹⁵M. G. Mason, C. W. Tang, L. S. Hung, P. Raychaudhuri, J. Madathil, L. Yan, Q. T. Le, Y. Gao, S.-T. Lee, L. S. Liao, L. F. Cheng, W. R. Salaneck, D. A. dos Santos, and J. L. Brédas, *J. Appl. Phys.* **89**, 2756 (2001).
- ¹⁶Q. T. Le, L. Yan, Y. Gao, M. G. Mason, D. J. Giesen, and C. W. Tang, *Appl. Phys. Lett.* **87**, 375 (2000).
- ¹⁷J. Kido and T. Matsumoto, *Appl. Phys. Lett.* **73**, 2866 (1998).
- ¹⁸E. I. Haskal, A. Curioni, P. F. Seidler, and W. Andreoni, *Appl. Phys. Lett.* **71**, 1151 (1997).
- ¹⁹X. Y. Deng, S. W. Tong, L. S. Hung, Y. Q. Mo, and Y. Cao, *Appl. Phys. Lett.* **82**, 3104 (2003).
- ²⁰X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, and K. Leo, *Appl. Phys. Lett.* **78**, 410 (2001).
- ²¹C.-C. Wu, C.-L. Lin, P.-Y. Hsieh, and H.-H. Chiang, *Appl. Phys. Lett.* **84**, 3966 (2004).