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Ultrathin Electron Injection Layer on Indium–Tin Oxide Bottom Cathode for Highly Efficient Inverted Organic Light-Emitting Diodes

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We have fabricated a highly efficient inverted bottom-emission organic light-emitting diode (IBOLED) based on an indium–tin oxide (ITO) bottom cathode deposited with an ultrathin 1 nm layer of Mg to promote electron injection. The threshold voltage of this IBOLED with a structure of ITO/Mg/Alq$_3$/NPB/WO$_3$/Al was 4.2 V and an efficiencies of 4.66 cd/A and 1.51 lm/W were achieved at an operational voltage of 8.9 V and a brightness of 940 cd/m^2. In comparison with an ITO/Alq$_3$ bottom cathode composition, a reduction in drive voltage from 13.8 to 7.8 V in voltage was obtained at 1 mA/cm^2. A charge-transfer dipole model is proposed to rationalize the enhanced electron injection. [DOI: 10.1143/JJAP.45.4948]

KEYWORDS: inverted organic light emitting device (IOLED), electron injection, indium tin oxide (ITO)

1. Introduction

Amorphous silicon (a-Si) thin-film transistors (TFTs) are emerging as a promising technology for the active-matrix organic light-emitting diode (OLED) backplane of large displays. The advantages of a-Si TFT backplane technology used to fabricate TFT liquid crystal display (TFT-LCD) panels could be extended to the manufacture of OLED displays. However, it is recognized that a-Si TFTs and conventional OLED architectures are not exactly compatible. The key component in conventional bottom-emitting OLEDs is composed of organic materials evaporated on a transparent indium–tin oxide (ITO) bottom anode followed by a coating of a reflective layer as the cathode. But, a-Si TFT technology usually features an n-channel TFT which necessitates the bottom contact of the OLED as the cathode and thus requires OLEDs to have an inverted structure as well. However, owing to its high work function, transparent ITO has been used mostly as the anode in conventional OLEDs for a variety of substrates.

A few groups have reported the use of reflective metal (MgAg[1] or Al[2–6]) as the bottom cathode and sputtered transparent ITO above the organic layers to make an up inverted top-emitting OLED (ITOLED). However, the intense radiation energy caused by sputtering may probably damage the organic layer in which gap states are created and induce further nonradioactive relaxation in injected carriers.[7] There have been few reports on protective capping layers used as buffers for reducing the radiation-induced damage caused by sputtering.[1,8–10] Replacing the top ITO anode with a thin film of Au,[11,12] NiO,[13] IZO,[14] or Ag/TeO$_2$[15] has also been shown to be effective in the fabrication of ITOLEDs. However, the variation of electroluminous (EL) spectra at different viewing angles caused by a microcavity effect owing to two opposite reflective metal/semi-transparent metal electrodes somehow limits the advantage of this approach.[16] Recently, inverted OLEDs have been developed rapidly and these achievements have attracted much interest. In this paper, we report on a highly efficient inverted bottom-emission OLED (IBOLED) using ITO as the bottom cathode. To the best of our knowledge, an IBOLED has not been reported in the literature. A high luminance efficiency of the IBOLED has achieved 4.66 cd/A at 20 mA/cm^2.

In general, the cathode and anode in OLEDs are required to have low and high work functions, respectively. Lower work function materials such as Ca, Mg, Yb,[17] Mg:Ag,[18] and LiF/Al[19] as the cathode can be made to inject electrons into the organic layer. By lowering the work function of the cathode metal, the quantum efficiency of the device is increased and operating voltage is decreased. Therefore, one of the major challenges in fabricating IBOLEDs is to prepare a bottom cathode with an effective electron injection using transparent ITO of high work function as the cathode.

Several mechanisms have been used to explain the enhanced electron injection originating from the lowering of the barrier height between the cathode Fermi level (E_F) and the lowest unoccupied molecular orbital (LUMO) of an organic material. One is a chemical reaction model,[20,21] in which the enhancement of electron injection is due to the formation of Alq$_3{}^-$ radical anions; the other is a dipole model in which the electric potential across the dipole layer reduces the interfacial barrier and accelerates carrier injection.[22,23] In this study, we show the performance of a series of IBOLED structures in which the electron-injection capability of the ITO cathode is compared by overcoating an ultrathin film of an electron-injecting tris-(8-hydroxyquinoline) aluminum (Alq$_3$)–LiF–Al trilayer,[7] LiF and Mg, and find ITO/Mg (1 nm) to be an excellent transparent cathode composition for IBOLEDs.

2. Experimental Details

The substrates used in this experiment were ITO-coated glass, and the thickness and sheet resistance of the ITO were 100 nm and 35 Ω/□, respectively. Prior to deposition, the ITO-coated glass substrates were cleaned by the general wet sequence procedure. Then these materials, Mg, organic materials and Al, were deposited by thermal evaporation at a vacuum of 10^{-6} Torr without breaking vacuum. The active area of the EL device, defined by the overlap of the ITO and the cathode electrodes, was 3×3 mm^2. The current density–voltage–luminance (*J*–*V*–*L*) characteristics of the devices were measured with a Photo Research PR650

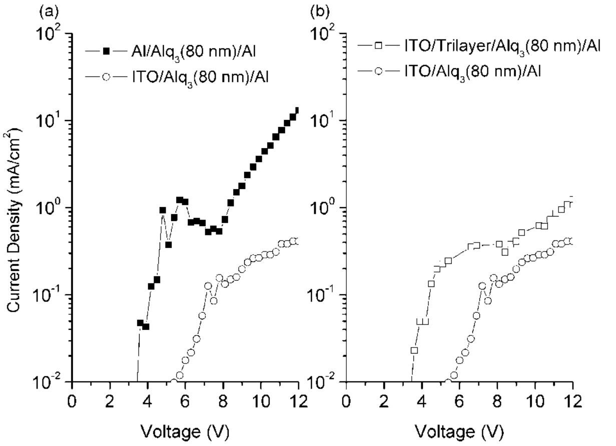

Fig. 1. *J–V* characteristics of electron only devices that use (a) Al or ITO, and (b) ITO as bottom cathode with and without ultrathin Alq$_3$–LiF–Al trilayer.

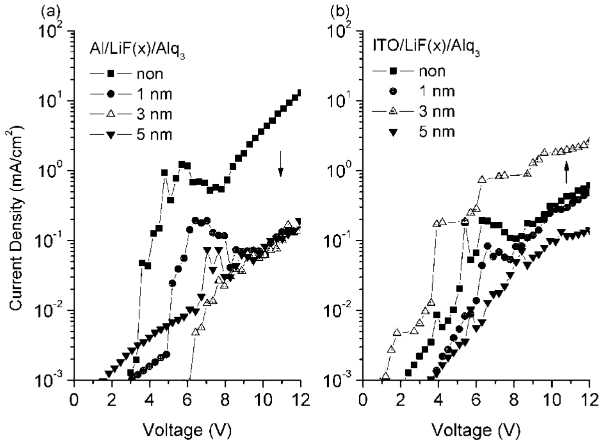

Fig. 2. *J–V* characteristics of LiF layer of different thicknesses inserted between bottom cathode and Alq$_3$: (a) Al as bottom cathode and (b) ITO as bottom cathode.

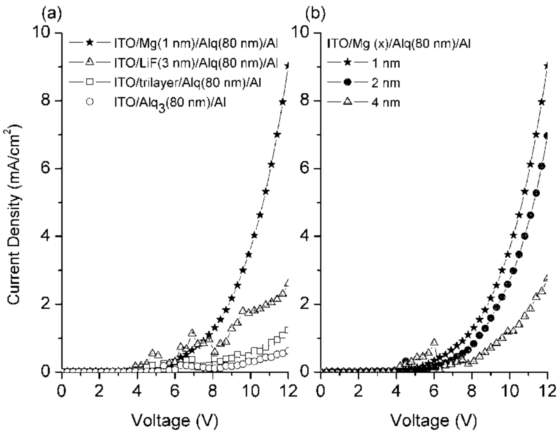

Fig. 3. Comparison of *J–V* characteristics of ITO with (a) trilayer, LiF and Mg as electron injection layers and (b) Mg different thicknesses deposited between ITO and Alq$_3$.

spectrophotometer and a computer-controlled programmable dc source (Keithley 2400).

3. Results and Discussion

In this study, electron-only devices were used to determine electron injection efficiency. Figure 1(a) shows the current denisty–voltage (*J–V*) characteristics of an electron-only device with the structure of cathode (ITO or Al)/Alq$_3$ (80 nm)/anode (Al, 100 nm) that measured the efficiency of electron injection from the bottom cathodes into the organic material Alq$_3$. Expectedly, owing to the higher work function of ITO (4.7 eV), the efficiency of electron injection of this device is found to be much lower than that of Al (as the bottom cathode), which has a work function of 4.2 eV.

Chen *et al.*[24] have reported the use of an ultrathin Alq$_3$–LiF–Al trilayer as an effective composite electron injection layer for the bottom Al and Ag cathodes in inverted top-emitting OLEDs. The chemical reaction for ultrathin Alq$_3$/LiF/Al trilayer electron injection is expressed as

$$3\mathrm{LiF} + \mathrm{Al} + 3\mathrm{Alq_3} \rightarrow \mathrm{AlF_3} + 3\mathrm{Li^+Alq_3^-},$$

in which [Li$^+$Alq$_3^-$] is believed to be the active injecting species.

However, we find the efficiency of electron injection by the Alq$_3$–LiF–Al trilayer has only a small improvement upon using ITO as the cathode; its is the worst when Al or Ag is used as the cathode. Figure 1(b) shows the results of a device with the structure of ITO substrate (cathode)/Alq$_3$–LiF–Al (trilayer)/Alq$_3$ (80 nm)/Al (100 nm, anode) in comparison with those of a device with the same structure but without the trilayer. Although it appeared that the trilayer increases the efficiency of electron injection in this configuration, we discovered that a more effective composition, as described below, is an ultrathin layer of Mg on ITO.

The optimized thickness of LiF inserted between Alq$_3$ and Al of the top cathode has been shown to be 1 nm in a conventional bottom-emitting OLED structure.[25] However, upon using Al as the bottom cathode in an inverted OLED configuration, it was found that the efficiency of electron injection decreased upon LiF deposition on the Al bottom cathode, but it was found that LiF did increase the efficiency of electrons injection from an ITO bottom cathode, as shown in Fig. 2. We conclude that LiF is not suitable for use in an Al bottom cathode even though Saheen *et al.*[26] have reported that LiF could reduce the work function of Al as a cathode.

We find that an ultrathin layer of magnesium (Mg) deposited on an ITO surface has the largest increase in electron injection efficiency of the materials tested [Fig. 3(a)]. Hiramoto *et al.*[27] used a Mg/ITO cathode to inject electrons into a t-BuPh-PTC organic layer. However, we find that the optimal thickness of Mg is only 1 nm, and thicker Mg does not produce a higher efficiency, as is shown in Fig. 3(b). Therefore, we suggest that the increase in efficiency is not due to Mg with a lower work function; rather, the results could be best rationalized by a charge-transfer-dipole model (Fig. 4). With a low coverage of Mg, the electrons of Mg can move in large numbers toward the ITO surface and can induce a charge-transfer dipole which in turn reduces the barrier height between ITO and Alq$_3$. Because the surface of ITO is not ideally flat, we think that 1 nm of Mg is insufficient to form an intimate contact monolayer on the surface. When the thickness of Mg increases gradually, the surface will be covered by a Mg thin

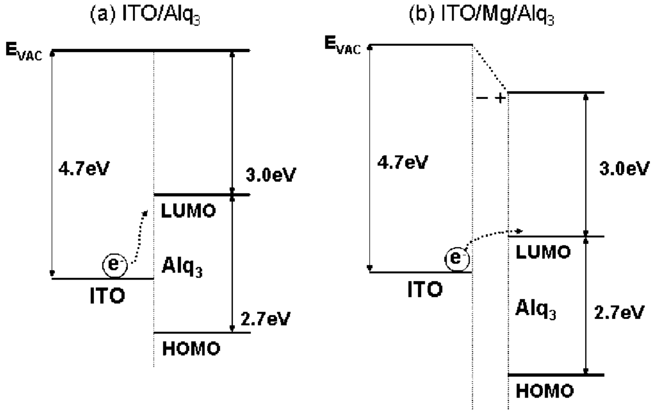

Fig. 4. Schematic diagram of energy levels of ITO/Alq_3 and ITO/Mg/Alq_3. (a) The initial electron injection barrier height is 1.7 eV between ITO and Alq_3, and (b) the barrier height can be reduced by the charge-transfer dipole.

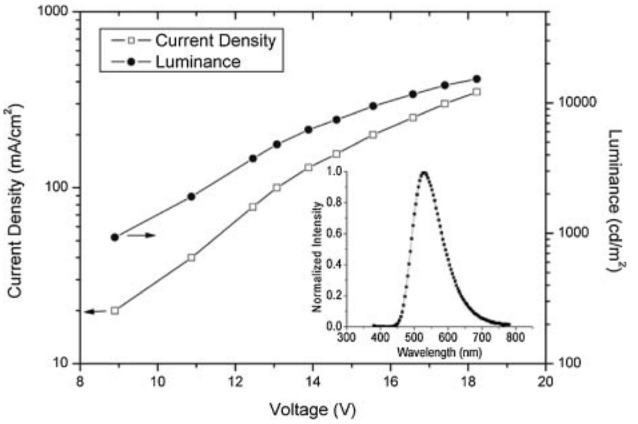

Fig. 5. *J–V–L* characteristics of inverted bottom-emitting device: ITO/Mg/Alq_3/NPB/WO_3/Al.

film that could suppress interfacial electron transfer and electronic interaction among Mg atoms. In comparison the reference electron-only device of [ITO/Alq_3/Al] with [ITO/Mg/Alq_3/Al] reduced drive voltage from 13.8 to 7.8 V at a current density of 1 mA/cm^2.

Finally, we have fabricated an inverted bottom-emitting device with the following composition: glass/ITO (cathode)/Mg (1 nm)/Alq_3 (60 nm)/NPB (60 nm)/WO_3 (5 nm)/Al (150 nm, anode). This device for electron injection from an ITO bottom cathode can be improved by adding a layer of 1 nm of Mg, and the efficiency of hole injection can be increased by optimizing the layer WO_3.[28,29] The threshold voltage of the IBOLED is 4.2 V. Figure 5 shows the *J–V–L* characteristics of this device, which achieves a luminous efficiency of 1.51 lm/W and a current efficiency of 4.66 cd/A at a drive voltage of 8.9 V and a current density of 20 mA/cm^2 producing a forward light output of approximately 940 cd/m^2. For benchmarking, this performance is slightly better than that of the conventional bottom-emitting OLED device with the structure of ITO (anode)/CuPc/NPB/Alq_3/LiF/Al (cathode), which has a driven voltage of 9.5 V at 20 mA/cm^2. Therefore, we believe that inverted bottom-emitting device described in this work has great potential to be integrated with a-Si TFT for application in large active-matrix OLED displays.

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