Air stable hybrid organic-inorganic light emitting diodes using ZnO as the cathode

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(Received 21 July 2007; accepted 22 October 2007; published online 26 November 2007)

An air stable hybrid organic-inorganic light emitting device is presented. This architecture makes use of metal oxides as charge injecting materials into the light emitting polymer, avoiding the use of air sensitive cathodes commonly employed in organic light emitting diode manufacturing. We report the application of zinc oxide as a cathode in an organic light emitting device. This electroluminescent device shows high brightness levels reaching 6500 cd/m^2 at voltages as low as 8 V. Compared to a conventional device using low workfunction metal cathodes, our device shows a lower turn-on voltage and it can operate in air. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2809387]

Organic light emitting diodes (OLEDs) are emerging as a next-generation technology for electronic displays and lighting. Apart from optimized device performances, the cost of production should be minimized to ensure the large scale applicability of the OLED technology in display and particularly lighting applications. With this respect it is of particular importance to be able to generate electroluminescence from devices using air stable charge injection interfaces. Such interfaces should not contain reactive metals or air sensitive charge injection layers. Recently, metal oxides have been employed with different characteristics and functions in OLED architecture.[1–4] However, the most appealing examples of the use of this class of compounds are as an alternative to low-workfunction materials commonly employed as cathode.[3,4] In those cases, titanium dioxide was chosen as the electron injection layer. Zinc oxide (ZnO) is another promising candidate for optoelectronic applications because of its suitable properties, such as high transparency, good electrical conductivity, tuneable morphology, and large variety of possible nanostructures.[5–7] Könekamp *et al.* showed an electroluminescent device where ZnO was used as near-UV emitter in combination with poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) as hole injection material.[8] However, ZnO has not been used as the cathode in OLEDs. Here, we report an air stable device using metal oxides both in electron and hole injection layers. In particular, the hybrid OLED (from now on, denominated as HyLED) is composed of a yellow-green light emitting polymer (LEP), poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT), sandwiched between a ZnO and a thin molybdenum oxide (MoO_3) layer (Fig. 1). In this case, the MoO_3 functions as the hole-injecting layer from the top Au electrode to the LEP.[9] It is important to underline that in this device architecture, the indium-tin oxide (ITO)-ZnO electrode is functioning as the cathode and the metal (Au) as the anode. In this inverted layout with respect to traditional OLEDs, no air sensitive metals or injection layers are employed, generating an, in principle, air stable device.

Thin ZnO films have been deposited by spray pyrolysis, which is a commonly used technique for the preparation of compact layers of many metal oxides.[10,11] We followed a procedure similar as reported earlier.[12,13] Briefly, zinc acetate dihydrate was dissolved in a mixture of ethanol and water (3:1). Acetic acid was added in order to avoid the formation of a white precipitate (zinc hydroxide [$Zn(OH)_2$]) and to enhance film deposition. This solution was sprayed onto prepatterned ITO glass plates (prior to deposition, the ITO-coated glass substrates were extensively cleaned, using chemical and UV-ozone methods) at 400 °C on a hot plate and the layers were subsequently annealed in a furnace at 500 °C for 12 h.

The morphology of the metal oxide layer has been investigated by atomic force microscopy. The surface must be flat in order to prevent shorts circuits between the metal oxide and the gold anode after polymer deposition. The analysis revealed that the surface of the ZnO layer is homogeneous and flat (Fig. 2), with a low roughness (rms of 6 nm). Therefore, we can reasonably assume that the oxide film is fully covered by the LEP layer (thickness of ~55 nm).

F8BT (ADS133YE, American Dye Source, Inc.) was spun on substrates from a chlorobenzene solution. Before spin coating the solutions were filtered over a 0.20 μm polytetrafluoroethylene filter. After LEP deposition, the thin films were dried at 85 °C for 15 min and then transferred to a high vacuum chamber integrated in an inert glove box atmosphere. MoO_3 and Au were thermally evaporated on the polymer layer under a base pressure of 1×10^{-6} mbar.

Thicknesses of the ZnO and spin coated LEP films were determined using an Ambios XP1 profilometer and are depicted in Fig. 1. The current-voltage (J-V) and electroluminescence-voltage characteristics were collected using a Keithley 2400 source measurement unit and a Si

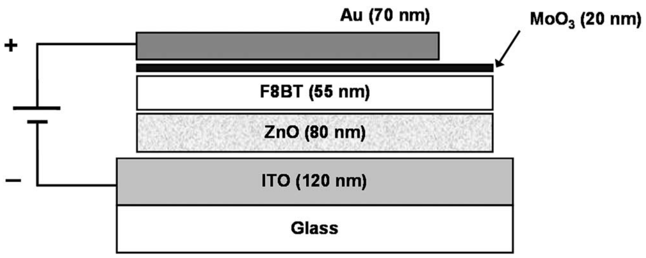

FIG. 1. Schematic device layout with indications of layer thickness.

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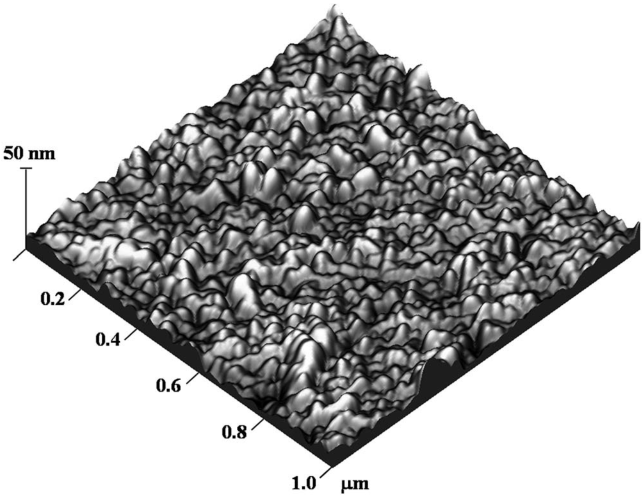

FIG. 2. Three-dimensional topography of a zinc oxide layer on ITO/glass substrate.

photodiode coupled to a Keithley 6485 picoamperometer, respectively. The photocurrent was calibrated using a Minolta LS100 luminance meter. Electroluminescence spectra were recorded using an Avantis fiber optics photospectrometer.

Current density and luminance versus applied voltage for an ITO/ZnO/F8BT/MoO_3/Au device are depicted in Fig. 3. Our HyLED shows a strong and uniform yellow-green luminescence (inset of Fig. 3), reaching brightness levels of 6500 cd/m^2 at 8 V.

The turn-on voltage for the luminance is very low, approximately 1.5 V, in accordance with the small build-in potential caused by the difference in energy between the conduction band of ZnO (−4 V) and the workfunction of gold (−5.4 V). However, the current onset occurs at a slightly lower voltage, indicating the preferential injection of one of the charge carriers. This delayed light output reflects the operational mechanism of the device. The incorporation of the thin MoO_3 layer in between the gold and the F8BT ensures the easy injection of holes.[14] Once injected, the holes are transported through the F8BT layer toward the negatively biased ZnO film. As the hole transport in F8BT is space charge limited,[15] an internal field is built up across the ZnO/F8BT interface facilitating the injection of electrons. The injection of electrons thus only occurs after the interfacial field has been created.

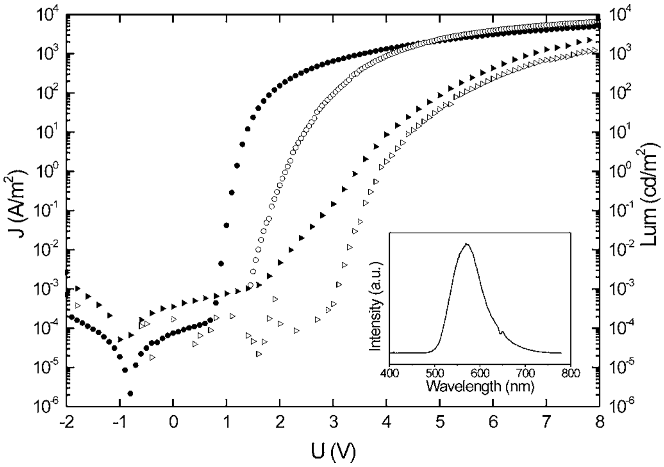

FIG. 3. Current density (full symbols) and luminance (open symbols) vs applied voltage for an ITO/ZnO/F8BT/MoO_3/Au device (circles) where ITO-ZnO is biased negatively and for a standard device ITO/PEDOT:PSS/F8BT/Ba/Ag (triangles) in which the ITO is biased positively. Inset shows the electroluminescence spectra recorded at 5 V.

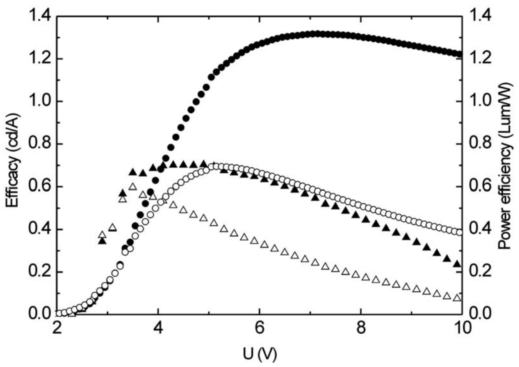

FIG. 4. Efficacy (full symbols) and power efficiency (open symbols) vs driving voltage for ITO/ZnO/F8BT/MoO_3/Au (circles) in which the ITO is biased negatively, and for a standard device ITO/PEDOT:PSS/F8BT/Ba/Ag (triangles) in which the ITO is biased positively.

To be able to compare the results obtained with our HyLED to OLEDs, a standard OLED device using barium as the cathode and F8BT as the active layer was prepared. A 100 nm PEDOT:PSS hole injection layer was deposited by spin coating from an aqueous dispersion. F8BT was spun over the PEDOT:PSS layer from a chlorobenzene solution and 5 nm of Ba and 80 nm of Ag were thermally evaporated on the LEP layer as the cathode.

As expected from the increased build-in potential, the reference OLED shows a higher turn-on voltage (~3 V). More surprisingly the light output of the F8BT OLED is lower than in our HyLED (Fig. 3). It should be noted that this is not the highest performance reported for a F8BT OLED; the difference is attributed to a slightly different device layout and perhaps to the F8BT purity. Although the efficacy of the HyLED is higher than that of the reference OLED (Fig. 4), its absolute value is somewhat disappointing when comparing it with the best values for polymer light emitting devices, especially in view of its impressive brightness. The main reason for the limited efficacy is the high current density flowing through the device. This current density is not related to leakage current, as is reflected by the rapid increase of the current density after the turn-on voltage (Fig. 3), but is most likely related to the recombination of holes and electrons, very close to or inside the ZnO layer.

In summary, we have demonstrated that the zinc oxide is a good candidate for the cathode material in HyLEDs, as such devices have luminance levels of one order of magnitude higher than that of devices using TiO_2 as the cathode.[3] This large difference in device performance depending on the type of metal oxide used is attributed to the nature of the metal oxide. Although the energies of the conduction band edges of TiO_2 and ZnO are similar, the most conductive form for ZnO is easier obtained. Undoped zinc oxide is a *n*-type semiconductor because of the presence of interstitial zinc and oxygen vacancies.[7,16] In our device architecture, these intrinsic defects in the ZnO lattice (induced by film annealing) introduce donor levels that can help electrons to overcome the energy gap between ITO and F8BT, enhancing the electron injection into the polymer. Further studies on the complete operational mechanism are currently being carried out.

This work has been supported by the European Union (HETEROMOLMAT, No. STRP 516982) the Spanish Ministry of Education and Science (MEC) (Nos. MAT2004-03849), and the Generalitat Valenciana. H.J.B. acknowledges the support of the Program "Ramon y Cajal" of the MEC.

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